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Evaluation of date seeds for oil extraction: effect of roasting on physico-chemical characteristics, antioxidant properties, oxidative stability, fatty acid profiles, and tocopherol compounds

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This study aims to investigate the effect of roasting on the quality of oils from three date seeds (*Degla Beida*, *Tanteboucht*, and *Deglet Nour*). To achieve this, unroasted and roasted (200°C for 22 min) date seeds were subjected to Soxhlet extraction, and the quality of the oils obtained was assessed by physico-chemical characterization (moisture, free fatty acids, peroxide value, K232, K270, colour, refractive index, and induction time), carotenoids and total phenolic contents (TPC), antioxidant activity (DPPH and ABTS), and fatty acid profile. The results showed that the roasting process significantly increased the oil yield, colour, and carotenoid and TPC compared to unroasted seeds. Furthermore, roasted seed oils also showed better antioxidant activity and revealed an elongation of the induction time by 1.5 to 3 times. However, the roasting led to a significant decrease in the total tocopherol contents, while the level of γ -tocopherol was strongly improved, with an increase of more than 80% for all roasted seed oils. In addition, the fatty acid profiles of oils were modified only slightly by the roasting process. These data demonstrate that the roasting of date seeds improves the nutritional value, antioxidant capacity, and thermo-resistance of their extracted oils.

Keywords: Date seed oil, Roasting, Quality parameter, Antioxidant property, Physico-chemical characteristic.

1. INTRODUCTION

The date palm (*Phoenix dactylifera* L.) represents an important fruiting plant for many countries and is renowned for its delicious and healthy date fruits [1,2]. The world production of date fruit was estimated to be 7715380 tonnes in 2021, from about twenty-five countries, of which Egypt was the leading producer, followed by Saudi Arabia and Iran [3].

In addition to the consumption of fresh dates, this fruit can be transformed into various processed forms, such as powders, date paste, syrup, juice, chocolate-coated dates, and date-based confectionery [4]. Most of the by-product resulting from these various transformations is made up of date pits or seeds and represent about 10 to 15% of the total weight of the date [5]. This by-product contains sugars (10.6-5.6%), of which 2.6-2.8% are ash, and proteins (5.4-4.0%), as well as numerous other bioactive compounds, particularly phenolic compounds recognized for their elevated antioxidant activity. It's also a very useful ingredient for preparing fibre-based foods due to the large amounts of dietary fibre, which represents about 15% [6].

Date seeds, containing 10 to 15% lipids, are the source of excellent oil [7], characterized by its high oxidative stability compared to numerous other vegetable oils [8]. As regards fatty acids composition, date seed oil is rich in oleic acid (25.89 to 55.10%) [9], which allows for better protection and resistance against deterioration in addition to the production of toxic products, such as

aldehydes, compared to other oils rich in linoleic and linolenic acids [10].

Date seed oil is a lucrative source of economic profit for the food industry, which has developed several fields in the formulation of added-value products. This oil is used in the production of mayonnaise [11], as natural antioxidants in oil blending, contributing to the enhanced stability of edible oil compared to synthetic substances [12], and can be added as a substitute for hydrogenated vegetable fats in the preparation of industrial products [13]. In addition, date seed oil is used in several non-food applications, such as cosmetic and pharmaceutical products [5].

Roasting is one of the thermal processes that treats food materials at high temperatures for a short period of time in order to enhance the quality of the products. The roasting process of oilseeds could improve the quality of oil by reducing moisture and increasing oil yield, bioactive compounds, antioxidant activity, and oxidative stability [14-16].

In this regard, this work seeks to evaluate the effect of roasting on the seed oils of three date varieties (*Degla Beida*, *Tanteboucht*, and *Deglet Nour*). The analyses were assessed by physico-chemical properties (moisture content, refractive index, acidity, UV absorption coefficient, peroxide value, and colour), bioactive compounds (total carotenoids, total phenolic contents), tocopherol and fatty acid compounds, oxidative stability, and antioxidant activity.

2. MATERIALS AND METHODS

2.1. DATE SEED SAMPLES

The fruits of three varieties of date palm, namely *Dagla Beida*, *Tanteboucht*, and *Deglet Nour*, were collected in 2021 from the Tolga region in the Biskra department, located in southeastern Algeria (34°43'18.5" N, 5°22'42.2" E). About 2 kg of pitted seeds were separated from date fruits. The seeds were soaked in water to eliminate any adhered date flesh and then wiped with absorbent paper.

2.2. DATE SEED ROASTING

The sample of each variety was divided into two parts, of which one portion was kept unroasted (control), and the other was subjected to roasting. The seeds were spread in a thin layer on trays and roasted at 200°C for 22 minutes [17] in a ventilated oven (Memmert UF110, Schwabach, Germany), then cooled to room temperature. The roasted and unroasted date seeds were ground into a fine powder (particle size < 250 µm) using a Fritsch Pulverisette 9 planetary ball mill (Pulverisette 5, Fritsch, Germany) and stored at -20°C in plastic sample bags until use.

The moisture content was determined by drying 5 g of powdered date seeds (roasted and unroasted) at

105°C in a ventilated oven until a constant weight was achieved [18]. The results were expressed as percentages.

2.3. OIL EXTRACTION

Twenty grams of each unroasted or roasted seed powder were subjected to oil extraction using a Soxhlet apparatus with n-hexane as solvent for 4 hours at a temperature of $68 \pm 3^\circ\text{C}$ [14]. The same procedure was repeated using 20 g of powder in each extraction until a volume of 50 mL of oil had been collected. The solvent was removed under vacuum using a rotary evaporator (Rotavapor R-210/215, Büchi, Switzerland) at 40°C, and the oils obtained were duly stored in darkness at 4°C until analysis. The yield was calculated using the following formula and expressed as a percentage of the initial dry weight of the seed powder.

$$\text{Oil yield (\%)} = (W_1/W_2) \times 100$$

where W_1 is the weight of the extracted oil and W_2 is the weight of the date seed powder (dry basis).

2.4. PHYSICO-CHEMICAL ANALYSIS

2.4.1 Refractive index

The refractive index (RI) was measured using an Anton Paar refractometer (Abbemat 3100, Germany). The measurements were taken at a temperature of 20°C, and the results were displayed directly by the apparatus.

2.4.2 Free fatty acids

The free fatty acids (FFA) were determined according to Kiritsakis and Markakis [19]. An aliquot of oil (5 g) was dissolved in previously neutralized ethanol and gently warmed. The resulting solution was titrated with NaOH solution (0.1 N) using phenolphthalein as a colouring indicator until a permanent light pink colour appeared. The content of FFA, expressed as a percentage of oleic acid, was calculated using the following formula:

$$\text{FFA (\%)} = (V \times N \times 282) / (10 \times m)$$

V : volume of NaOH titrant (mL), N : Normality of NaOH (0.1 N), 282: Molecular weight of oleic acid (g/mol), m : Sample mass in grams.

2.4.3 UV absorption coefficient

The UV absorption coefficients (K232 and K270) were determined on the basis of the absorption of a 1% solution of oil in cyclohexane (w/v) at 232 and 270 nm [14].

2.4.4 Peroxide value

The peroxide value (PV) was determined using the

method described by Novidzro et al. [20]. A 5g aliquot of sample was mixed with 18 mL of acetic acid and 12 mL of chloroform. Then, 1 mL of a saturated solution of potassium iodide (KI) was added to this mixture. After 5 min in the dark, 75 mL of distilled water was added and vigorously stirred with the addition of a few drops of starch solution as a colouring indicator. The resulting solution was titrated with sodium thiosulfate solution (0.01 N) until the colour disappeared. The PV was calculated using the following formula:

$$PV \text{ (meq g/ kg)} = (N \times (V - V_0) \times 1000) / m$$

Pv: Peroxide value expressed as milliequivalent grams O₂ per kilogram of oil (meq O₂/Kg),

N: Normality of Na₂S₂O₃ solution, V: Volume of Na₂S₂O₃ used in titration, V₀: Volume of Na₂S₂O₃ used in blank titration, m: Sample mass in grams.

2.4.5 Carotenoids

The concentration of carotenoids was determined using the method described by Isabel Minguez-Mosquera et al. [21]. For 0.6 g of oil sample, 2 mL of cyclohexane was added, and the resulting mixture was thoroughly agitated. The absorbance was measured at 470 nm using UV/Vis spectroscopy according to the following formula.

$$\text{Carotenoid (mg/kg)} = \frac{A \times 10^6}{2000 \times 100 \times d}$$

A: absorbance at 470 nm; 2000: specific extinction of lutein, the predominant compound in the carotenoids fraction; d: the thickness of the spectrophotometer cell. The concentration of carotenoids was expressed as milligrams per kilogram of oil (mg/kg).

2.4.6 Colour

The colour of the oils was measured according to ISO 15305 (1998) using Lovibond (Tintometer, PFX 880 Series). Results were expressed in terms of red and yellow values.

2.4.7 Fatty acids composition

The fatty acids of the unroasted and roasted date seed oils were identified and quantified according to Mohd Jaih et al. [23] with certain modifications. Initially, methyl esters were prepared using methanolic boron trifluoride (13-15%), then a volume of 1 µL was injected into a gas chromatography system (6890 Network GC System, Agilent Technologies, USA) equipped with a Flame Ionization Detector (FID). The system was equipped with a capillary column (60 m × 0.25 mm internal diameter × 0.25 µm film thickness) and an injector spraying at a temperature of 250°C. The temperature gradient was programmed to increase by 6.5°C/min from 130°C to 170°C and

then by 40°C/min from 170°C to 230°C. Hydrogen was used as the carrier gas, and the fatty acids were identified and quantified as a relative percentage by correlating the retention time and peak area with the FA methyl ester standards.

2.5. DETERMINATION OF TOTAL PHENOLIC CONTENT

The TPC was measured using the method described by Mohd Jaih et al. [23]. First, the oils were diluted in dimethyl sulfoxide (DMSO). Then, 0.5 mL of the diluted oil was mixed with 2.5 mL of 10% Folin-Ciocalteu reagent and 2 mL of 7.5% sodium carbonate. The resulting mixture was incubated for one hour at 40°C. The absorbance was read at 765 nm. Gallic acid was used as a reference and the results were given as milligrams of gallic acid equivalent per 100 g of oil (mg GAE/100 g).

2.6. ANTIOXIDANT ACTIVITY

Antioxidant activity was evaluated using two methods: the DPPH (1,1-diphenyl-2-picrylhydrazyl) and ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) assays. The DPPH assay was carried out according to Bondet et al. [24]. Various concentrations of date seed oil solutions were prepared using dimethyl sulfoxide (DMSO). Then, 0.2 mL of each extract was mixed with 2 mL of a methanolic DPPH radical solution (0.025 mg/mL), and the mixture was shaken vigorously before being left to stand at room temperature for 30 min. The absorbance was measured at 517 nm. The results were given as a half-efficient concentration (IC₅₀) and expressed as mg/g.

The ABTS radical scavenging activity evaluation was described by Re et al. [25]. A mixture of aqueous solutions of potassium persulfate (2.45 mM) and ABTS (7 mM) was stored for 16 h in the dark to create the stock solution composed of ABTS radical cations (ABTS^{•+}). Then, the solution was diluted with ethanol to obtain an absorbance of 0.7±0.03 at 765 nm. The unroasted and roasted seed oils of the three date varieties were diluted with DMSO at different concentrations. Subsequently, 100 µL of each oil dilution was mixed with 2.9 mL of the prepared ABTS^{•+} solution. The results were given as half-efficient concentrations (IC₅₀) and expressed as mg/g.

Additionally, butylated hydroxytoluene (BHT) and ascorbic acid were used as reference antioxidants in both DPPH and ABTS assays to evaluate and compare the antioxidant activity of the oils. Their IC₅₀ values were determined under the same experimental conditions as the samples to ensure consistent comparison.

2.7. TOCOPHEROL ANALYSIS

Tocopherols were analyzed by high-performance liquid

chromatography (HPLC) aided by a fluorescence detector (Jasco, Japan) [26]. An aliquot of oil was mixed with 10 μ L of tocopherols as internal standards in hexane. The solution was centrifuged at 3500 rpm/5 min, and the supernatant was analyzed by HPLC. The column used for separation was Supelcosil™ LC-SI. For the elution, a 97:3 hexane:dioxane mixture was used at a flow rate of 1.0 mL/min for 12 min. The results were analyzed with the ChromNAV Control Center - JASCO Chromatography Data Station (Japan). Authentic standards were used for comparison, identification, and quantification. The results were expressed in mg/kg of oil.

2.8. OXIDATIVE STABILITY

The seed oils were analyzed by the 743 Rancimat analyzer (Metrohm AG, Herisau, Switzerland) according to the procedure of Benbouriche et al. [27]. A 3 g aliquot of date seed oil was tested at a temperature of 100°C at an airflow rate of 15 L/hour. The data were expressed in hours as an induction time (IT).

Statistical analysis

The results were expressed as the mean $\pm$ standard deviation of the three replicates. The data were compared statistically by analysis of variance following the LSD (Least Significant Difference) test using Statistica 5.5. The comparison of means before and after roasting was carried out by the Student t-test. The level of significance was taken at $p < 0.05$. The graphs were generated using Microsoft Excel.

3. RESULTS AND DISCUSSION

This study was conducted to evaluate the effect of roasting on the quality and antioxidant properties of seed oils of three date varieties (*Degla Beida*, *Tantebouchet*, and *Deglet Nour*). The photographs of date seeds and their corresponding powders and extracted oils before and after roasting are shown in Figure 1.

3.1. MOISTURE OF DATE SEEDS

The results of moisture contents of the three varieties before and after roasting are indicated in Table I. The moisture contents of unroasted date seeds were higher (6.21-6.87%) than of roasted ones (1.03-1.49%). These values were in agreement with those of many unroasted seed varieties of Saudi Arabia [11] Tunisia [28,29], and United Arab Emirates [30], which were between 3.66 and 10.3%. The difference in moisture content depends on several factors, including the growing region, variety [31], as well as pretreatments such as drying and roasting. The moisture content of seeds was significantly reduced by approximately 5 times for all varieties after the roasting process. These results were similar to those reported by Rahman et al. [4] for Tamr variety roasted at 220°C for 15-20 min.

3.2. OIL YIELD

The oil yield could be dependent on different growth conditions, harvest stages, and raw material sources

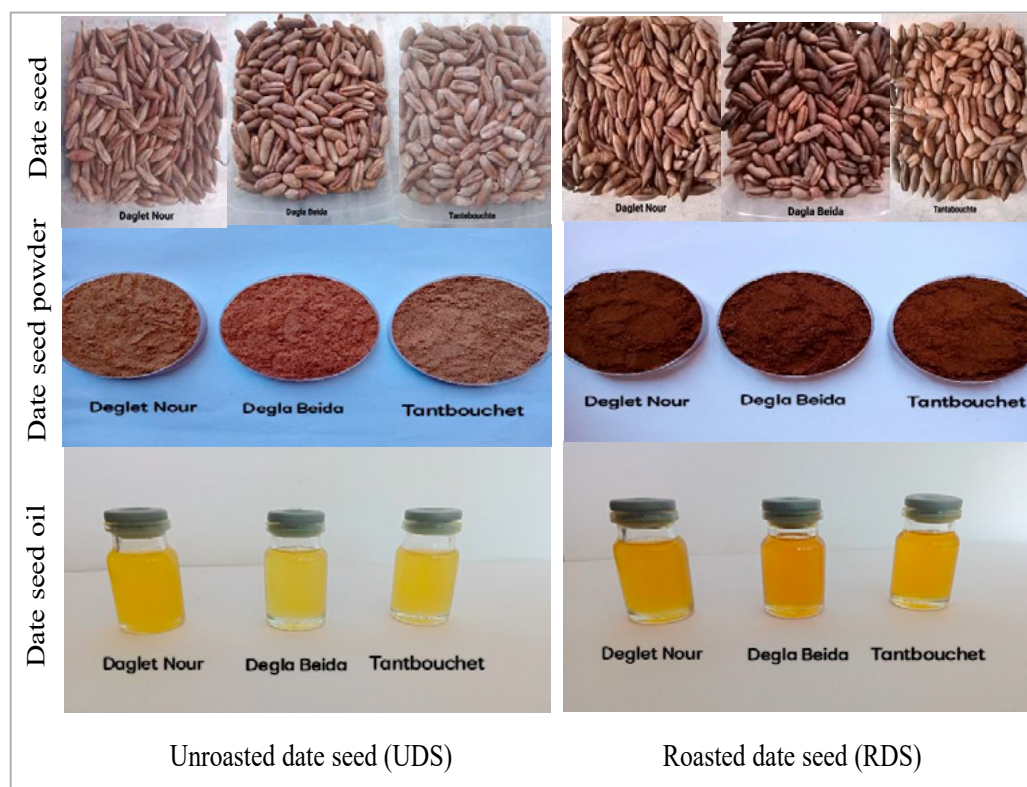


Figure 1 - Photographs of seeds, powders, and oils of unroasted and roasted date seeds.

such as the region and the variety. Date seeds may contain between 3 and 16.5% oil [9].

The results of the oil yields of the studied varieties are presented in Table I. It was observed that oil yields were very close for the three unroasted date seeds, with an average of 9.65%, and also for the roasted seed oils, with about 10.23%. The roasting induced a significant increase in oil yield for all varieties, with 10% for *Degla Beida* and 4% for *Tanteboucht* and *Deglet Nour*.

These results were higher than those for Algerian unroasted seed varieties with 4.1-4.93% [32], and similar to the results obtained in some other investigations into unroasted date seeds with yields ranging from 7 to 10% [33,34]. The increase in the oil yield after roasting was supported by other studies. It was found that roasting increased the yield by 75% with an increment in roasting temperature [35]. This positive effect of roasting on oil yield was related to the release of oil by breaking down the cell structure through the heating process and to the generation of pores in the oil-seed structures, facilitating the movement of oil from the seed to the outside [36].

3.3. REFRACTIVE INDEX

The refractive index provides information on the quality and purity of oils and fats, which increase with the length of the chain and the amount of unsaturated fatty acids. RI depends on the type of oil, its origin, the technological treatments, and the oxidative status [37]. Table I presents the refractive index results of the unroasted and roasted oils studied. The unroasted seed oils have a RI ranging from 1.4502 to 1.4612.

The roasting did not affect the RI of the seed oils of the three varieties. These findings were in agreement with unroasted seed oil from Tunisian date varieties [8]. Nor were any effects observed of roasting of coconut (*Cocos nucifera*) seed oil and Soxhlet and cold press extraction oils from chia seeds [38,39], but the RI slightly decreased for sunflower oils with the roasting time of sunflower seeds and gradually decreased for sesame oils with the increase in roasting temperature of sesame seeds [40,41].

3.4. FREE FATTY ACIDS

The amounts of the FFA of unroasted and roasted date seed oils are given in Table I. The results before roasting elucidated regular FFA contents for UDB, UT, and UDN (0.11-0.15%) and didn't show significant differences. Low acidity levels were also obtained from date seed oils of Saudi Arabia cultivars (0.360-0.676%) [11,42].

The free fatty acid content of oils significantly increased from an average of 0.13% before roasting to 0.66% after roasting, but these values remained relatively weak and were included in the recommended standards. Edible oils typically have FFA values below 0.5% for refined oils, while higher FFA content (up to 5% or more) may be acceptable in crude or unrefined oils [43]. Significantly, RDN (0.60%) was the least affected and showed the least content compared to RDB and RT. The increase of acidity with roasting was due to the release of fatty acids due to hydrolysis of triglycerides caused by heating (200°C). Similar findings were seen in different studies into the effect of seeds roasting on oil acidity, including chia and argan seeds [39,44].

Table I – Physico-chemical parameters of unroasted and roasted date seeds and seed oils

Varieties	<i>Degla Beida</i>		<i>Tanteboucht</i>		<i>Deglet Nour</i>	
Parameter	UDB	RDB	UT	RT	UDN	RDN
Seeds						
Moisture	6.34 ± 0.15 ^b	1.32 ± 0.11 ^{a ↓}	6.87 ± 0.09 ^a	1.49 ± 0.10 ^{a ↓}	6.21 ± 0.08 ^b	1.03 ± 0.07 ^{b ↓}
Oil yield	9.52 ± 0.41 ^a	10.49 ± 0.38 ^{a ↑}	9.79 ± 0.19 ^a	10.17 ± 0.13 ^{a ↑}	9.65 ± 0.19 ^a	10.03 ± 0.11 ^{a ↑}
Oils						
RI	1.450 ± 0.05 ^a	1.460 ± 0.10 ^{a /}	1.461 ± 0.04 ^a	1.463 ± 0.07 ^{a /}	1.453 ± 0.08 ^a	1.461 ± 0.06 ^{a /}
FFA	0.15 ± 0.03 ^a	0.71 ± 0.03 ^{a ↑}	0.13 ± 0.02 ^a	0.72 ± 0.02 ^{a ↑}	0.11 ± 0.05 ^a	0.60 ± 0.04 ^{b ↑}
K232	1.62 ± 0.10 ^a	1.98 ± 0.08 ^{a ↑}	1.55 ± 0.08 ^{ab}	1.89 ± 0.04 ^{ab ↑}	1.45 ± 0.06 ^b	1.81 ± 0.09 ^{b ↑}
K270	0.34 ± 0.04 ^b	1.03 ± 0.05 ^{a ↑}	0.66 ± 0.06 ^a	1.05 ± 0.08 ^{a ↑}	0.59 ± 0.03 ^a	1.09 ± 0.07 ^{a ↑}
PV	3.97 ± 0.12 ^b	4.79 ± 0.10 ^{a ↑}	4.43 ± 0.10 ^a	3.70 ± 0.22 ^{b ↓}	3.92 ± 0.07 ^b	3.68 ± 0.13 ^{b ↓}
Carotenoids	1.24 ± 0.03 ^c	7.66 ± 0.08 ^{a ↑}	1.95 ± 0.02 ^a	5.10 ± 0.05 ^{c ↑}	1.50 ± 0.01 ^b	7.40 ± 0.04 ^{b ↑}
Color						
Red unit	3.40 ± 0.17 ^a	5.50 ± 0.16 ^{a ↑}	3.20 ± 0.10 ^a	4.40 ± 0.21 ^{b ↑}	3.40 ± 0.12 ^a	4.40 ± 0.11 ^{b ↑}
Yellow unit	7.30 ± 0.15 ^b	24.00 ± 0.97 ^{b ↑}	6.70 ± 0.27 ^b	28.00 ± 1.17 ^{a ↑}	14.00 ± 1.37 ^a	26.10 ± 1.39 ^{ab ↑}

U, unroasted; R, roasted; DB, *Degla Beida*; T, *Tanteboucht*; DN, *Deglet Nour*; The results are expressed as the mean ± SD; The results in the same row for roasted or unroasted seeds with different letters are statistically different (ANOVA, LSD test, P<0.05); The results of roasted seeds with the signs ↑, /, or ↓ are statistically higher, similar, or lower compared to unroasted seeds of the same variety (Student t-test, P<0.05).

3.5. UV ABSORPTION COEFFICIENT

The oxidation of unsaturated fatty acids leads to the formation of peroxides, which are the primary oxidation products associated with the formation of conjugated dienes. The increase in these products indicates an increase in ultraviolet absorption at 232 nm. UV absorption at 270 nm indicates the generation of conjugated trienes and secondary oxidation products [45].

The results of K232 showed a significant difference only between DB and DN before and after roasting (Table I). The results of K270 revealed a lower value for UDB compared to UT and UDN, while the results for roasted varieties were similar. The roasting affected the absorptivity of oils, where significant increases in UV absorption at both 232 and 270nm were found, with increases of 22.22, 202.94, and 21.94% for K232 and 59.09, 24.83, and 84.75% for K270 for seed oils of the *Degla Beida*, *Tanteboucht*, and *Deglet Nour*, respectively. Similar studies demonstrated that roasting leads to an increase in the formation of conjugated dienes and trienes in peanut oil [46], argan oil [44], and rapeseed oil [47].

3.6. PEROXIDE VALUE

The unroasted seed oils of the three varieties showed a low peroxide value (3.92-4.43 meq O₂/kg) with the highest value found for the *Tanteboucht* variety (Table I). Regarding the results of the effect of roasting seeds

on oils, the PV was slightly increased for *Degla Beida* seed oil (from 3.97 to 4.79), whereas it was reduced for *Tanteboucht* (from 4.43 to 3.70) and *Deglet Nour* (from 3.92 to 3.68) seed oils. The increase observed in PV is due to the oxidation of unsaturated fatty acids, while the decrease can be attributed to its decomposition into secondary products of oxidation under high temperature. Several studies have reported that the PV of roasted seed oils first increases at low temperatures and then decreases at high temperatures [48,49]. Overall, the results of the peroxide value for all varieties were below the maximum recommended value of 15 meq/kg [50].

3.7. CAROTENOID CONTENTS

Carotenoids are beneficial components due to their important physiological properties, and they play an important role in oxidative stability due to their antioxidant capacity. They are commonly used in industry as colouring additives [51,52].

The carotenoid contents before and after heat treatment of the three date seed oils are presented in Table I. The level of carotenoid in unroasted seed oils ranged from 1.24 to 1.95 mg/kg. In other works on the oils of unroasted date seeds, the carotenoid contents were 11.24 mg/kg for the Tunisian date of Kentichi variety [53], from 11.8 to 26.8 mg/kg for United Arab Emirates date varieties [54], and from 17.57 to 12.35 mg/kg for Moroccan varieties [55].

Table II - Fatty acid composition of unroasted and roasted date seed oils

Varieties	<i>Degla Beida</i>		<i>Tanteboucht</i>		<i>Deglet Nour</i>	
Fatty acid	UDB (%)	RDB (%)	UT (%)	RT (%)	UDN (%)	RDN (%)
C8:0	0.38 ± 0.08 ^b	0.39 ± 0.05 ^{a/}	0.5 ± 0.02 ^a	0.41 ± 0.01 ^{a/}	0.40 ± 0.04 ^b	0.49 ± 0.02 ^{a/}
C10:0	0.40 ± 0.08 ^b	0.42 ± 0.05 ^{b/}	0.58 ± 0.02 ^a	0.50 ± 0.02 ^{ab/}	0.48 ± 0.04 ^b	0.58 ± 0.02 ^{a/}
C12:0	21.47 ± 2.63 ^c	21.92 ± 2.16 ^{c†}	24.70 ± 0.39 ^a	23.89 ± 0.41 ^{b†}	23.78 ± 1.06 ^b	24.45 ± 0.19 ^{a†}
C14:0	11.75 ± 0.5 ^a	11.74 ± 0.64 ^{a/}	10.75 ± 0.06 ^c	11.21 ± 0.07 ^{b†}	11.52 ± 0.02 ^b	10.46 ± 0.03 ^{c↓}
C16:0	11.18 ± 0.34 ^a	11.01 ± 0.05 ^{a↓}	9.21 ± 0.05 ^c	9.33 ± 0.09 ^{b†}	9.40 ± 0.36 ^b	9.24 ± 0.01 ^{b/}
C18:0	3.6 ± 0.29 ^a	3.68 ± 0.2 ^{a/}	3.29 ± 0.05 ^b	2.90 ± 0.04 ^{c↓}	2.89 ± 0.23 ^c	3.41 ± 0.02 ^{b↓}
C20:0	0.46 ± 0.04 ^a	0.46 ± 0.05 ^{a/}	0.47 ± 0.01 ^a	0.40 ± 0.04 ^{a/}	0.39 ± 0.04 ^a	0.49 ± 0.01 ^{a/}
C22:0	0.28 ± 0.02 ^a	0.29 ± 0.04 ^{a/}	0.3 ± 0.02 ^a	0.28 ± 0.02 ^{a/}	0.26 ± 0.08 ^a	0.36 ± 0 ^{a†}
C18:1	42.81 ± 0.07 ^b	42.19 ± 1.71 ^{c↓}	42.55 ± 0.29 ^c	43.48 ± 0.41 ^{a†}	43.75 ± 1.91 ^a	42.83 ± 0.2 ^{b†}
C18:2	7.50 ± 0.2 ^a	7.46 ± 0.29 ^{a/}	7.19 ± 0.03 ^b	6.94 ± 0.02 ^{c↓}	6.78 ± 0.16 ^c	7.24 ± 0.07 ^{b↓}
C18:3	0.35 ± 0.03 ^b	0.35 ± 0.03 ^{a/}	0.42 ± 0.01 ^{ab}	0.47 ± 0.03 ^{a/}	0.47 ± 0.03 ^a	0.45 ± 0.01 ^{a/}
C22:2	0.15 ± 0.01	0.17 ± 0.01 ^{a/}	/	0.17 ± 0.03 ^a	/	/
SFA	49.51 ± 2.6 ^b	49.91 ± 2.57 ^{a†}	49.80 ± 0.36 ^a	48.93 ± 0.44 ^{c↓}	49.12 ± 0.59 ^c	49.48 ± 0.29 ^{b↓}
UFA	50.81 ± 0.31 ^b	50.16 ± 2.01 ^{c↓}	50.16 ± 0.33 ^c	51.07 ± 0.39 ^{a†}	51.00 ± 2.1 ^a	50.52 ± 0.28 ^{b†}
PUFA	8.00 ± 0.24 ^a	7.97 ± 0.3 ^{a/}	7.61 ± 0.04 ^b	7.58 ± 0.15 ^{c/}	7.25 ± 0.19 ^c	7.69 ± 0.08 ^{b↓}
MUFA	42.81 ± 0.07 ^b	42.18 ± 1.68 ^{c↓}	42.55 ± 0.29 ^c	43.48 ± 0.41 ^{a†}	43.74 ± 1.95 ^a	42.83 ± 0.2 ^{b†}
UFA/SFA	1.03 ± 0.06 ^a	1.00 ± 0.09 ^{a/}	1.01 ± 0.01 ^a	1.04 ± 0.01 ^{a/}	1.04 ± 0.05 ^a	1.02 ± 0.01 ^{a/}

U, unroasted; R, roasted; DB, *Degla Beida*; T, *Tanteboucht*; DN, *Deglet Nour*; SFA, saturated fatty acid; UFA, unsaturated fatty acid; PUFA, polyunsaturated fatty acid MUFA, monounsaturated fatty acid. The results in the same row for roasted or unroasted seeds with different letters are statistically different (P<0.05). The results of roasted seeds with the signs †, /, or ↓ are statistically higher, similar, or lower compared to unroasted seeds of the same variety (P<0.05).

The total carotenoid content in the oils of roasted seeds was significantly increased, reaching levels of between 5.10 and 7.66 mg/kg, with *Dagla Beida* seed oil displaying the highest amount. Previous studies showed comparable results in the case of nigella seed oil [49] and rapeseed oil [47]. Increased pigment levels may be due to the breakdown of complexes between proteins and pigments after protein denaturation with heating [56].

3.8. COLOUR

The colour results of oils extracted from unroasted and roasted date seeds are shown in Table I. According to the data, the roasting of seeds increased both the red and yellow colours of all seed oils. Some phenolics, chlorophylls, and carotenoids are the main compounds responsible for oil colouration; the increase in the latter after the roasting process may be attributed to release of these compounds as well as the compounds produced by the Maillard reaction, such as pyrazines and melanoidins, during the roasting process at high temperature [57].

3.9. FATTY ACID COMPOSITION

The fatty acid compositions of unroasted and roasted seed oils of the three varieties are summarized in Table II. Regarding unroasted seed oils, the most dominant fatty acid was oleic acid (C18:1), which ranged between 42.55 and 42.81%, followed by lauric (C12:0), myristic (C14:0), and then palmitic (C16:0) acid. The erucic acid (C22:1) was detected only in UDB seed oil; the remainder of the fatty acids were present only in low amounts. These oils were classified in the category of oleic-lauric oils, as established by previous investigations [28,32,58]. Other classifications were proposed by numerous investigators, such as the oleic-myristic oil type [54], and the oleic-linoleic category [59].

The unsaturated fatty acid/saturated fatty acid (UFA/SFA) ratios of seed oils ranged from 1.007 to 1.03, indicating an approximate equivalence between the amounts of saturated and unsaturated fatty acids. These results overall were in agreement with those reported previously [32,60,61]. However, this ratio was lower compared to other vegetable oils such as olive (3.00) and sesame (4.18) oils [62].

The fatty acid compositions of the three seed oils were slightly modified by the roasting process. According to other investigations, the fatty acid compositions of okra, rice germ, and peanut oils were not affected by roasting [63-65].

3.10. TOTAL PHENOLIC CONTENT

Phenolic compounds are bioactive substances with important antioxidant properties due to their ability to scavenge free radicals and reactive oxygen species [66]. The total phenolic content obtained from the

unroasted and roasted date seed oils is presented in Figure 2. For the unroasted seed oils, the TPC of UDB oil (17.89 mg/100 g oil) was significantly higher, followed by UT oil and then UDN seed oil. The results obtained were lower than those found by Harkat et al. [32] for the same Algerian varieties, which ranged between 154.59 and 193.35 GAE mg/100 g, while the results of this study are higher than those reported by Rakhshanda et al. [67] for unroasted seeds oil of the Pakistan date variety (3.641 mg/100 g). Similarly, the seed oils of two Tunisian date cultivars, Deglet Nour and Allig, exhibited TPC levels of 52.6 mg/100 g and 21.5 mg/100 g, respectively [68].

For the roasted seeds, the TPC in RDB seed oil was significantly higher compared to RT seed oil, followed by RDN seed oil. The TPC of these oils were more than double that of unroasted seed oils. From the previous results, it can be seen that the roasting process positively affected the TPC of oils extracted from roasted seeds. It has been demonstrated that both the roasting temperature and duration significantly enhance the total phenolics of the extracted oil. Raising the roasting temperature from 160 to 200°C resulted in a 43% increase in oil phenolics after 30 minutes of date seed roasting. Moreover, extending the roasting time from 10 to 30 minutes led to a 39% increase in the oil's TPC [17]. This enhancement is mainly attributed to thermal processes such as the breakdown of lignocellulosic structures and protein denaturation, which improve the extractability of phenolic compounds. Furthermore, the Maillard reaction contributes to the formation of phenolic-type structures, including proanthocyanidins and gallic acid [69], thereby amplifying the phenolic content. Similar observations have also been reported during the roasting of other seeds, including gourd seed oil [15], cactus seed oil [70], and sesame seed oil [14].

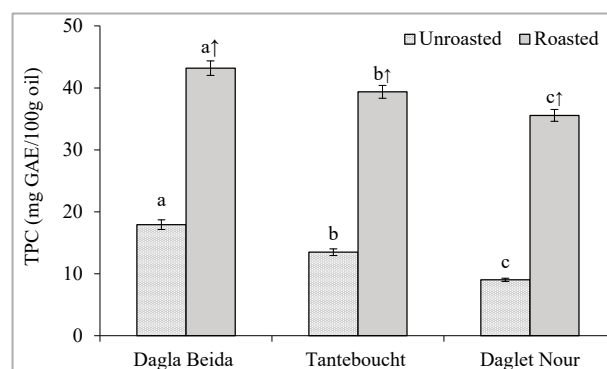


Figure 2 - TPC of unroasted and roasted seed oils.

The results for roasted or unroasted seeds with different letters are statistically different ($P < 0.05$). The results of roasted seeds with the signs ↑, /, or ↓ are statistically higher, similar, or lower compared to unroasted seeds of the same variety ($P < 0.05$).

3.11. ANTIOXIDANT ACTIVITY

In this study, the antioxidant activity was estimated by measuring the concentration of inhibition to scavenge 50% of free radicals, known as IC₅₀, which was estimated through two methods based on the scavenging of DPPH (1,1-diphenyl-2-picrylhydrazyl) and ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) free radicals. A lower value of IC₅₀ signifies the highest antioxidant capacity, and the opposite is true for a high value.

The results obtained for these analyses are given in Figure 3. The antioxidant activity of seed oils assessed by both DPPH and ABTS methods revealed significantly higher inhibition potential for UDB (165.65 and 244.54 mg/mL, respectively), followed by UT, then UDN. These results are roughly similar to those found for unroasted seed oils of Algerian date varieties, which were between 170 and 330 mg/mL for the DPPH method [71].

Moreover, the roasting of seeds had a positive effect on the antioxidant activity of the oils compared to unroasted seeds. RDB seed oil exhibited the highest anti-radical efficiency against DPPH and ABTS, with respective concentrations of 67.50 and 76.8 mg/mL, the latter recorded for RDN seed oil. It was noticed that the IC₅₀ decreased by more than half compared to that of the unroasted seeds, and this can be attributed to the TPC, carotenoids, and other compounds formed during roasting. Similar enhancements in antioxidant activity following roasting have been reported for apricot kernel oil [72], peanut oil [73], and Sacha-Inchi oil [48].

However, compared to pure synthetic standards, the antioxidant activity of both oils remained lower than that of BHT and ascorbic acid, which exhibited IC₅₀ values of 13.53 and 4.87 µg/mL, respectively, in the DPPH assay, and 7.26 and 2.18 µg/mL, respectively, in the ABTS assay. This difference can be attributed to the higher purity and reactivity of synthetic antioxidants, which are specifically designed to neutralize free radicals more efficiently than natural oil extracts.

Therefore, based on the previous findings, roasting date seeds not only increases the phenolic compound content in the oils but also significantly boosts their antioxidant activity. In particular, the antioxidant activity of date seed powder, assessed using the DPPH radical scavenging assay, nearly doubled when the roasting temperature increased from 160 to 200°C after 20 minutes of roasting [17]. This improvement was probably due to enhanced phenolic release resulting from cell wall degradation, as well as the formation of antioxidant Maillard reaction products such as melanoidins. Specifically, pyrazines are compounds formed during roasting through Maillard reactions, which involve the interaction between amino acids and reducing sugars. These compounds not only contribute to the characteristic roasted aroma but also exhibit antioxidant activity. Recent studies have confirmed that pyrazines are generated via these pathways and play a role in enhancing the antioxidant properties of roasted foods [74,75].

3.12. TOCOPHEROL CONTENT

Tocopherols include four types of isomers (α, β, γ, and δ). They are known as important dietary factors for some physiological processes and for their antioxidant properties in lipophilic media [76]. The individual and total tocopherol content of unroasted and roasted seed oils are reported in Table III. The three isomers of tocopherols detected in each date seed oil were α, γ and δ, while β-tocopherol was not detected. Oils obtained from unroasted seeds exhibited total tocopherol content ranging from 634.77 to 1939.6 mg/kg. α-tocopherol was the most abundant compared to the other isomers. *Deglet Nour* seed oil showed the highest amount of α-tocopherol (1679.25 mg/kg), which represents 86.25% of the total tocopherols, followed by *Tanteboucht* and *Degla Beida* seed oils with 56.93 and 68.14%, respectively. The γ-tocopherol contributed approximately 5% to 22% of total tocopherols, with the lowest value found in *Deglet Nour* seed oil (93.49 mg/kg). δ-tocopherol represented about 9

Table III - Tocopherol composition (mg/kg) and Rancimat induction time (h) of date seed oils before and after roasting process.

Varieties Parameters	<i>Degla Beida</i>		<i>Tanteboucht</i>		<i>Deglet Nour</i>	
	UDB	RDB	UT	RT	UDN	RDN
TTC	634.77 ± 4.23 ^c	590.91 ± 4.35 ^{a↓}	914.9 ± 4.11 ^b	562.66 ± 4.73 ^{b↓}	1939.6 ± 3.23 ^a	461.57 ± 4.23 ^{c↓}
α-tocopherol	361.41 ± 3.60 ^c	263.10 ± 3.72 ^{a↓}	623.5 ± 3.48 ^b	203.59 ± 5.24 ^{c↓}	1679.25 ± 2.72 ^a	230.10 ± 3.60 ^{b↓}
γ-tocopherol	138.90 ± 22.72 ^b	299.47 ± 6.72 ^{a↑}	165.82 ± 5.48 ^a	302.72 ± 6.60 ^{a↑}	93.49 ± 4.72 ^c	178.15 ± 2.48 ^{b↑}
δ-tocopherol	152.5 ± 6.36 ^b	53.32 ± 2.61 ^{a↓}	102.31 ± 3.36 ^c	56.35 ± 2.36 ^{a↓}	166.86 ± 2.24 ^a	28.34 ± 6.60 ^{b↓}
IT (h)	21.54 ^b	61.61 ^{a↑}	29.68 ^a	47.42 ^{b↑}	20.27 ^c	37.74 ^{c↑}

U, unroasted; R, roasted; DB, Degla Beida; T, Tanteboucht; DN, Deglet Nour. The results in the same row for roasted or unroasted seeds with different letters are statistically different (P<0.05). The results of roasted seeds with the signs ↑, /, or ↓ are statistically higher, similar, or lower compared to unroasted seeds of the same variety (P<0.05). IT, induction time; TTC, total tocopherol contents

to 24% of the total tocopherols. The results were within the range of those found for α and γ -tocopherols in the unroasted seed oil of ten date varieties, with 248.17-1584.57 mg/kg and 36.75-272.92 mg/kg, respectively [77]. Similar results were also recorded for total tocopherols ranging from 560.12 to 946.26 mg/kg compared to those of the *Degla Beida* and *Tanteboucht* in this study [32].

The results obtained indicated that the roasting process influenced date seed oils. The total, α - and δ -tocopherol contents were significantly decreased for all analyzed oils after roasting, while the level of γ -tocopherol was significantly increased by more than 80% for all roasted seed oils. The increase in the amount of γ -tocopherol can be explained by the rupture of bonds established with gamma-tocopherol with proteins of the membranes, phosphates, and/or phospholipids through the roasting treatment [78]. A reduction was displayed in the amount of α -tocopherol in peanut oils after the roasting process, while γ -tocopherol was not changed significantly [73]. γ -tocopherol content in sesame seed oil showed an increase after roasting up to a temperature of 200°C but decreased using a higher temperature (220°C) [79]. Additionally, the effect of the microwave after 15 minutes of roasting sunflower seeds induced a decrease in the amount of α -tocopherol, but the δ -tocopherol was completely degraded [40]. Other studies also reported a decrease in the level of total tocopherols in sesame oil with the duration of roasting [44,80]. Therefore, the choice of temperature and duration of seed roasting is important to preserve the tocopherols of the extracted oils from degradation.

3.13. RANCIMAT INDUCTION TIME

The oxidative stability of oils and lipids is an important quality indicator; it is related to the resistance to temperature and oxygen and depends on the composition of antioxidants such as tocopherols, polyphenols, carotenoids, and mainly on fatty acid and triglyceride profiles. Among the most widely used methods to determine oxidative stability, the Rancimat test is one of the methods that efficiently assesses oxidation by measuring induction time over high temperatures (50 to 220°C) [81].

The results of the Rancimat test of unroasted and roasted seed oils of the three varieties are represented in Table III. The induction time (hours) is measured at 100°C with an air supply of 15 L/h. The results of unroasted seed oils showed that the highest IT was recorded for *Tanteboucht*, followed by *Dagla Beida*, and finally *Daglet Nour*. Similar results were reported for unroasted dates seed oil from the Saudi Arabia variety [42]. However, in a previous study a higher IT was reported for unroasted seed oil of the *Deglet Nour* variety (45 h) [8].

The influence of roasting treatment on date seeds led to an enhanced induction time for the three varieties; the IT of *Dagla Beida* seeds oil increased up to 61.61 h, *Tanteboucht* seeds oil up to 47.42 h, and *Daglet Nour* up to 37.74 h. This significant increase can be explained by the high content of phenolic antioxidants responsible for the amelioration of IT after seed roasting, despite the degradation of tocopherols. Indeed, the IT of virgin olive oil presented a strong correlation with total polyphenols ($r = 0.97$), while no significant correlation was seen with tocopherol content ($r = 0.05$) [82]. In another study, only a weak correlation ($r = 0.383$) was observed between total tocopherol concentrations and IT in various types of edible oils [83]. The IT of oil is not only attributed to the fatty acid composition but also to the contents of antioxidant compounds, including phenolic compounds, carotenoids, and tocopherols [84].

Several studies corroborate the results obtained by demonstrating a positive effect of seed roasting on the oxidative stability of their oils, such as peanut seed oil [64], argan seed oil, gurun seed oil [15,85], sunflower, and rapeseed seed oils [86].

4. CONCLUSIONS

In this study, three date varieties (*Dagla Beida*, *Tanteboucht*, and *Deglet Nour*) were chosen in order to assess the effect of seed roasting on the quality of extracted oils. The roasting treatment significantly increased the oil yield and enhanced the levels of bioactive compounds (carotenoids and phenolic compounds). Moreover, this treatment improves antioxidant activity, the time of oxidation induction, with no effect on the fatty acid composition. Among the three varieties, the roasted *Degla Beida* seeds oil was selected since it had the best characteristics. This study demonstrated that roasting date seeds had a positive impact on the nutritional value and oxidative stability of the oils obtained. Unroasted date seed oils, rich in native phenolics and unsaturated fatty acids, may therefore be candidates for applications in nutraceutical or cosmetic formulations. Roasted date seed oils, benefitting from their enhanced antioxidant properties, could be used as natural stabilizers in functional foods and dietary supplements to improve shelf life and nutritional quality.

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Conflict of interest

The authors declare that they have no conflicts of interest.

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Reg. UE 2022/2104 and 2022/2105 establish the chemical-physical parameters and methods for quality control of olive oil.

The organoleptic assessment (Panel test) contributes to the definition of the quality of the oil, the Regulation classifies virgin olive oil in the categories:

- EXTRA VIRGIN OLIVE OIL
- VIRGIN OLIVE OIL
- LAMPANTE OLIVE OIL

according to the intensity of the defects and of the fruitiness perceived, as determined by a group of tasters selected, trained and monitored as a panel, using statistical techniques for data processing. It also provides information on the organoleptic characteristics for optional labeling. The organoleptic assessment is qualified by a level of reliability comparable to that of the analytical tests.

Our Panel is recognized by the IOC (International Olive Council), by the Italian Ministry of Agricultural, Food and Forests as a tasting committee in charge of the official control of the characteristics of virgin olive oils and designation of origin (D.O.) oils.

The organoleptic assessment is accredited by ACCREDIA (Italian Accreditation Body).

The Panel serves industry, production consortia, certification bodies and large-scale distribution.



Virgin Olive Oil Organoleptic Assessment



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Expert Sensorial Analysis and Head of Panel Test
Team Chemistry, Technology and Food Safety

Assessment of nutritional quality indices of lipids in whole organism, flesh, and shell of *Pandalus borealis* consumed in Nigeria

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Classic fatty acid indices, nutritional quality indices and crude fats were determined, calculated and reported in this work as obtained from the body parts (whole organism, flesh and shell) of *Pandalus borealis* shrimp. The range of the crude fat (CF) was 0.80 to 1.31 g/100 g with corresponding edible portion (EP/100 g) 0.53 to 1.02 g/100 g. The energy density was low at 29.6 to 48.5 kJ/100 g (19.5 to 37.6 kJ/100 g) in CF/EP/100g or 7.20 to 11.8kcal/100g (4.75 to 9.14 kcal/100 g) in CF/EP/100 g. The classic fatty acid indices were (% of total fatty acids); reporting range values: $\sum$ SFA (18.3 to 19.6%), $\sum$ MUFA (29.2 to 40.6%), trans fatty acids, $\sum$ TFA (9.00E-5 to 1.50E-4%), $\sum$ n-6 PUFA (23.1 to 24.0%), $\sum$ n-3 PUFA (16.7 to 18.5%), $\sum$ n-6+ $\sum$ n3 - PUFA (39.8 to 42.0%), $\sum$ UFA (71.2 to 81.8%), EPA (5.80 to 8.87%) and DHA (8.88 to 11.4%). Nutritional quality indices reported were: PUFA/SFA; atherogenicity index (AI), thrombogenicity index (TI), hypocholesterolemic/hypercholesterolemic ratio (HH), unsaturation index (UI), health-promoting index (HPI), EP-A+DHA, fish lipid quality/flesh lipid quality (FLQ) and peroxidizability index (PI). Most of the nutritional quality indices values were of health-promoting results, e.g. AI (0.13 to 0.14) were better than Eskimo diet (0.39); TI (0.21 to 0.24) were better than Eskimo diet (0.28), n-6/n-3 (1.27:1 to 1.38:1) were better than (4:1 to 10:1) and close to PUFA/SFA of ≥ 0.40 (1.0-1.5) with values ranging from 2.03 to 2.28. *Pandalus borealis* shrimp body parts produced low $\sum$ SFA, low energy, insignificant $\sum$ TFA, high $\sum$ UFA, and favorable nutritional health quality indices.

Keywords: *Pandalus borealis*, Low energy density, nutritionally favorable health quality indices.

1. INTRODUCTION

According to Wikipedia [1], a shrimp (PL: shrimp or shrimps) is a crustacean (a form of shellfish) with an elongated body and a primarily swimming mode of locomotion – typically belonging to the Caridea or Dendrobranchiata of the decapod order, however, some crustaceans outside of this order are also referred to as “shrimp”. In a broader definition, shrimp may be synonymous with prawn, referring to stalk-eyed swimming crustaceans with long whiskers (antennae) and slender legs [2]. Any small crustacean that resembles a shrimp tends to be called one [3]. They swim forward by paddling with swimmerets (pleopods) on the underside of their abdomens. Shrimps have thin, fragile legs which they use primarily for perching [3].

Bauler [4], in his book titled “Remarkable Shrimps: Adaptations and Natural History of Carideans”, characteristically explained both shrimp and prawn as follows. *Shrimp* is characteristically used to refer to those crustaceans with long antenna, smaller legs and a laterally compressed, muscular abdomen that is highly adapted for both a forward and backward (retrograde) escape response. *Prawn* is often used as a synonym of *shrimp* for penaeoidean and caridean shrimp,

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especially those of large size. The English Oxford Dictionaries provide the following definitions [5].

Shrimp: a small free-swimming crustacean with an elongated body, typically marine and frequently of commercial importance as food.

Prawn: a marine crustacean which resembles a large shrimp [6].

Historically, it was the distinction between walking and swimming that formed the primary taxonomic division to the former suborders Natantia and Reptantia. Members of the Natantia (shrimp in the broader sense) were adapted for swimming, while the Reptantia (crabs, lobsters, etc.) were adapted for crawling or walking [4]. Many shrimp species are small as the term *shrimp* suggests, about 2 cm (0.79 in) long, but some shrimp exceed 25 cm (9.8 in). Larger shrimps are often referred to as prawns.

Shrimp have a widespread habitat: they are found close to the seafloor of coasts and estuaries, rivers and lakes. Species are numerous and they may be adapted to a particular habitat [3]. Most shrimp species are marine, although about a quarter of the species described are found in fresh water [7]. Marine species are found at depths of up to 5000 meters (16000ft) [8], from the tropics to the polar regions. Two species of *Merguia* are known to be semi-terrestrial and spend a significant part of their life on land on mangrove [9,10].

Decapods were traditionally grouped into two suborders: Natantia (or swimmers) and Reptantia (or walkers). Natantia included the shrimp. Natantia was thought to be paraphyletic, that is, it was thought that originally all decapods were like shrimp [11].

Classifications are now based on clades, and the paraphyletic suborder Natantia has been discontinued. On this basis, taxonomic classifications now divide the order Decapoda into two suborders: Dendrobranchiata for the largest shrimp clade, and Ploecyemata for all other decapods. The Ploecyemata are in turn divided into half a dozen infra-orders [11].

- The taxonomists De Grave and Fransen [12] recognize four major groups of shrimps: the suborder Dendrobranchiata and the infra-orders Procarididea, Stenopodidea and Caridea. This contains decapods only and is identical to the traditional Natantia group.

- All shrimp of commercial interest belong to the Natantia. The FAO determines the categories and terminology used in the reporting of global fisheries. They define a shrimp as a “decapod crustacean of the suborder Natantia” [13].
- According to the Codex Alimentarius Commission of the FAO and WHO: “The term *shrimp* (which includes the frequently used term prawn) refers to the species covered by the most recent edition of the FAO listing of shrimp, FAO Species Catalogue, Volume 1[14]. The Species Catalogue states that the highest category it deals with is “the suborder Natantia of the order Crustacean Decapoda to which all shrimps and prawn belong” [15].

The following Table IA contains the principal commercial shrimp, the seven most harvested species; all of them are Decapods [1]. Group: Dendrobranchiata

The main use of shrimp in SE Asia is in the production of shrimp paste, a fermented product that goes under names such as *blachan* (Malaysia and Indonesia) [37]. *Blacang* (also spelled as *blachan*), is the Malay and most common name for SE Asian fermented shrimp paste, which is called *terasi* or *trasi* in Indonesia, *kapi* in Thailand, and *bagoong* in the Philippines. The paste referred to as *balichko* in Macao is similar. A form of *blacang* is also found in Burma and Sri Lanka [38]. The Indo-Pacific species described as having ‘commercial importance’, i.e. sought by fishermen and regularly sold in markets, include a few genera such as *Acetes* and *Caridina* [37]. Potted shrimp is a delicacy in England, as described by Dorothy Hartley [39]. Shrimp paste is also an English favorite; however, it is quite different from the fermented shrimp paste of SE Asia [37]. Most shrimp are sold frozen and marketed based on their categorization of presentation, grading, color and uniformity [40]. Shrimp is generally sold whole, though sometimes only shrimp meat is marketed. Shrimp has high levels of omega-3 fatty acids and low levels of mercury [41]. Shrimp is high in calcium, iodine and protein, but low in energy. Shrimp meal is also a significant source of cholesterol, from 122 mg to 151 mg/100 g of shrimp, depending on the method of preparation [42]. Even with these cholesterol levels, shrimp consumption is considered healthy for the circulatory system

Table IA – Principal commercial shrimp species

Common name	Scientific name	FAO	WoRMS
Whiteleg shrimp	<i>Litopenaeus vannamei</i> (Boone 1931)	16, 17	18
Giant tiger prawn	<i>Penaeus monodon</i> (Fabricius 1798)	19, 20	21
Akiami paste shrimp	<i>Acetes japonicus</i> (Kishinouye 1905)	22, 23	24
Southern rough shrimp	<i>Trachysalambria curvirostris</i> (Stimpson 1860)	25, 26	27
Flesh prawn	<i>Fenneropenaeus chinensis</i> (Osbeck 1765)	28, 29	30
Bana prawn	<i>Fenneropenaeus merguensis</i> (De Man 1888)	31, 32	33
Northern prawn	<i>Pandalus borealis</i> (Krøyer 1838)	34, 35	36

because the lack of significant levels of SFA in shrimp means that its high cholesterol content actually improves the ratio of LDL to HDL cholesterol and lowers triglycerides [43].

This study concerns one major commercial shrimp named *Pandalus borealis*. The fact sheet on *Pandalus borealis* is as follows.

Classification:

Biota

- Animalia (Kingdom)
- Arthropoda (Phylum)
- Crustacea (Subphylum)

Multicrustacea (Superclass)

- Malacostraca (Class)

Eumalacostraca (Subclass)

- Eucarida (Superorder)
- Decapoda (Order) [Latreille 1802]
- Pleocyemata (Suborder)
- Caridea (Infraorder)

Pandaloidea (Superfamily)

- Pandalidae (Family)
- *Pandalus* (Genus)
- *Pandalus borealis* (Species)

Environment: marine

Original description Krøyer, H. (1838) [44].

Descriptive notes: Distribution: Greenland to Martha's Vineyard, Massachusetts. Widely fished since 1900s in Norway, and later in other countries following Johan Hjort's practical discoveries of how to locate them. They have a short life, which contributes to a variable stock on a yearly basis. They are not considered over-fished [1].

Maximum length (mm): 165

Depth (m): 20 – 1380 [34, 35, 36].

2010 production (thousand tonnes):

- wild = 361
- farmed = –
- total = 361

Taxonomic citation: DecaNet eds. [45]

Status: Accepted

Rank: Species

Parent: *Pandalus* (Leach 1814)

Original name: *Pandalus borealis* (Krøyer 1838)

Previous studies on the anatomical part of *Pandalus borealis* have been reported. Adeyeye [46] reported the amino acid profile of the whole organism, flesh and shell of *Pandalus borealis* (Krøyer 1838). The report showed the total amino acid values as 86.6 to 93.0 g/100 g; the total essential amino acid range was 37.9 to 40.9 g/100 g cp (42.9 to 44.0%); cysteine/total sulfur amino acid, the Cys/TSAA range was 1.98 to 17.5; predicted protein efficiency ratio (P-PER): P-PER1 (1.21 to 1.71), P-PER2 (1.65 to 2.12); essential amino acid index, EAAI (79.5% to 99.4%); biological value, BV (75.0% to 96.6%); Lys/Trp (3.05 to 62.5) and Met/Trp (2.54 to 37.8). Adeyeye [47] also

reported the classic fatty acid indices, while providing an in-depth discussion of this subject. In this report, the major discussion is based on an assessment of the nutritional quality indices of lipids in whole organism, flesh and shell of *Pandalus borealis* consumed in Nigeria. This report assists in predicting the health status on the consumption of *Pandalus borealis* fat.

2. MATERIALS AND METHODS

Shrimps caught from fresh marine water, brackish water, and ponds of various types have become delicacies in Nigeria. They are eaten either whole (shell + flesh) after drying or as flesh (when fresh) [47]. The body of the shrimp is divided into two main parts: the head and thorax, which are fused together to form the cephalothorax, and a long narrow abdomen. The shell that protects the cephalothorax is harder and thicker than the shell elsewhere on the shrimp and is called the carapace. The carapace typically surrounds the gills, through which water is pumped by the action of the mouth parts [8].

2.1. COLLECTION AND TREATMENT OF SAMPLES PRIOR TO ANALYSES

Wet samples were collected from trawler catches from Idumota (along the Lagos Atlantic Ocean). The shrimps were washed with distilled de-ionized water and drained under folds of filter paper. Samples were collected in crushed ice in insulated containers and brought to the laboratory for preservation. The washed shrimp were wrapped in aluminum foil and kept in the laboratory refrigerator (2.8°C) pending analyses. Sample identification occurred before preservation.

2.2. SAMPLE PREPARATION FOR ANALYSES

On removal from the laboratory refrigerator, defrosting was allowed to occur for about one hour. Whole shrimps were beheaded and the outer shells removed. The various parts were dried at 105°C and blended in a blender after reaching constant drying weight. The three distinct samples were whole organisms (head + flesh + shell), flesh (endoskeleton only), and shell (head + body shell).

2.3. CRUDE FAT DETERMINATION

About 0.25 g of each aliquot was weighed in the extraction thimble and the fat extracted with petroleum ether (40 to 60°C boiling range) using a Soxhlet apparatus [47]. The extraction process lasted 5-6 h. Determinations were in duplicate.

2.4. PREPARATION OF FATTY ACID METHYL ESTERS (FAMES) AND ANALYSES

The crude fat extracted was converted to methyl ester using the boron trifluoride method [47]. The gas

chromatographic conditions for the analysis of fatty acids methyl esters were as follows:

GC: HP5890 powered with HP ChemStation rev. A09.01 [1206] software;

*injection temperature: split injection;

*split ratio: 20:1;

*carrier gas: nitrogen; inlet temperature: 250°C;

*column type: HP INNOWAX; column dimensions: 30 m x 0.25 mm x 0.25 µm;

*oven program: initial temperature at 60°C: first ramping at 10°C/min for 20 min (260°C), maintained for 4 min; second ramping at 15°C/min for 4 min (320°C), maintained for 10 min;

*detector: flame ionization detector (FID); detector temperature: 320°C;

*hydrogen pressure: 22 psi; compressed air: 35 psi. The peaks obtained were identified by comparison with standard fatty acid methyl esters. Determinations were in duplicate.

2.5. QUALITY ASSURANCE

For the purpose of ensuring the accuracy of the obtained results, the following actions were performed: standard chromatograms were prepared for the fatty acids methyl esters, which were then compared with the respective analytical result; calibration curves were prepared for all the standard mixtures and the correlation coefficient was determined for each fatty acid parameter (31 in number). The correlation coefficient value should be ≥ 0.95 for the result to be acceptable. This is a statistical index that shows the quality assurance of the preformed calibration curve. It was performed using Hewlett Packard Chemistry (HPCHEM) software [47].

2.6. FATTY ACIDS CALCULATED AS EDIBLE PORTION

Fatty acids were listed with the chain length and double bond numbers. At the data source and reference data base levels, values for individual fatty acids are usually expressed as a percentage of total fatty acids since this is the most common forms of analytical presentation. At the user base level, values per 100 g of food are required. At all levels of data management both modes of expression are useful for comparative evaluation. A conversion factor derived from the proportion of the total lipids present as fatty acids is required [47] for converting percentages of total fatty acids to fatty acids per 100g of food.

2.7. FATTY ACID AND QUALITY PARAMETERS

Lipids possess characteristic fatty acid composition and consequently influence health outcome. Fatty acids play critical roles in human metabolism, health, and diseases. Fatty acids are associated with cardiovascular diseases [48, 49, 50], neurological diseases [51, 52], fatty liver diseases (non-alcoholic) [52], allergic diseases [54], etc.

2.8. NUTRITIONAL INDICES

2.8.1 Polyunsaturated fatty acid/saturated fatty acid ratio (PUFA/SFA)

The PUFA/SFA ratio represents an index usually used to assess the impact of diet on cardiovascular health (CVH). It estimates how all PUFAs in the diet can depress low-density lipoprotein cholesterol (LDL-C) and lower levels of serum cholesterol and how all SFAs contribute to high levels of serum cholesterol. Hence, a higher PUFA/SFA ratio denotes a more positive effect [55].

SFAs responsible for raising serum cholesterol are C12:0, C14:0 and C16:0, thereby inhibiting the activity of low-density lipoprotein receptors (LDLRs); C18:0 appeared to be biologically neutral because it can easily be metabolized to oleic acid and has no effects on circulating LDL-C levels [56].

The PUFA/SFA circulating formula is:

$$\sum \text{PUFA} / \sum \text{SFA} \quad (1)$$

2.8.2 Atherogenicity index (AI)

Ulbricht and Southgate [57] developed this index, which characterizes the atherogenic potential of fatty acid. The AI indicates the relationship between the sum of SFAs [C12:0, C14:0 and C16:0] that are considered pro-atherogenic (i.e. they favor the adhesion of lipids to cells of the circulatory and immunological systems) [58] and UFAs that are considered to be anti-atherogenic, as they inhibit the accumulation of plaque and reduce levels of phospholipids, cholesterol and esterified fatty acids [58]. Hence, consumption of diets of products with low AI can reduce the levels of total cholesterol and LDL-C in human blood plasma [59].

The formula for calculating AI is:

$$\text{AI} = [\text{C12:0} + (4 \times \text{C14:0}) + \text{C16:0}] / \sum \text{UFA} \quad (2)$$

2.8.3 Thrombogenicity index (TI)

Both the index of thrombogenicity (IT) and index of atherogenicity (IA) were developed by Ulbricht and Southgate [57]. This index characterizes the thrombogenic potential of fatty acids, predicting the tendency to form clots in blood vessels, and provides the contribution of different fatty acids, which denotes the relationship between the pro-thrombogenic fatty acids [C12:0, C14:0, C16:0] and the anti-thrombogenic fatty acids (MUFAs, the n-3 and n-6 PUFA families) [57]. Foods or products with low TI are beneficial for CVH. The TI formula is:

$$\text{TI} = [\text{C14:0} + \text{C16:0} + \text{C18:0}] / [(0.5 \times \sum \text{MUFA}) + (0.5 \times \sum \text{n-6 PUFA}) + (3 \times \sum \text{n-3 PUFA}) / (\text{n-3/n-6})] \quad (3)$$

2.8.4 Hypocholesterolemic/hypercholesterolemic (HH) ratio

The HH ratio is an index used in the fatty acid profile of lamb meat. It was first proposed by Santos-Silva

et al [60]. SFA is high in lamb leading to a low value of PUFA/SFA. The HH ratio characterizes the relationship between hypocholesterolemic fatty acid (cis-C18:1 and PUFA) and hypercholesterolemic fatty acid. Since no C12:0 was detected in the lamb meat, Santos-Silva et al. [60] concluded that the formula only includes C14:0 and C16:0 in hypercholesterolemic fatty acid. Mierliță [61] later optimized the formula by adding C12:0 in hypercholesterolemic fatty acid in studies of sheep milk. The formula is:

$$HH (cis-C18:1 + \sum PUFA) / (C12:0 + C14:0 + C16:0) \quad (4)$$

2.8.5 Health-promoting index (HPI)

HPI is the inverse of AI. The index was proposed by Chen et al [62]. It is currently mainly used in research on dairy products such as milk [62] and cheese [62].

$$\sum UFA / [C12:0 + (4 \times C14:0) + C16:0] \quad (5)$$

2.8.6 Unsaturation index (UI)

Different unsaturated fatty acids have different weights in the UI, which indicates the impact of highly unsaturated fatty acid. Therefore, UI indicates the degree of unsaturation in lipids and is calculated as the percentage of each unsaturated fatty acid multiplied by the number of double bonds within that fatty acid [63]. The calculation formula is:

$$UI = 1 \times (\% \text{monoenoics}) + 2 (\% \text{dienoics}) + 3 \times (\% \text{trienoics}) + 4 \times (\% \text{tetraenoics}) + 5 \times (\% \text{pentaenoics}) + 6 \times (\% \text{hexaenoics}) \quad (6)$$

2.8.7 Sum of eicosapentaenoic acid and docosahexaenoic acid (EPA + DHA)

Both EPA and DHA are n-3 long-chain (LC) PUFAs that play important roles in the human body; these include a reduction in the risk of CVD, hypertension and inflammation. DHA is an important (essential) component of the retina, neuronal system, visual functioning and cognitive functioning in humans [64].

2.8.8 Fish lipid quality/flesh lipid quality (FLQ)

The main aim of FLQ calculation is similar to the EPA + DHA index, which calculates the sum of EPA and DHA as a percentage of total fatty acids. For accurate calculation of FLQ, it would be necessary to know the EPA% (of total FAs) and DHA% (of total FAs) conversion to edible portions per 100 g, i.e. EPA% (-EP/100 g) + DHA (-EP/100 g). FLQ was originally used for fish lipid quality [65] or flesh lipid quality [66]. The formula is:

$$FLQ = 100 \times (C22:6n-3 + C20:5n-3) / \sum FA \quad (7)$$

2.8.9 Linoleic acid/ α -linolenic acid (LA/ALA) ratio

This ratio [LA, C18:2n-6/ α - linolenic acid (ALA, C18:3n-3)] was developed for guiding infant formula. Tissues of adults have a lower rate of synthesis of n-3 long-chain PUFAs than those of infants, hence

the LA/ALA ratio in the diet does not have much of an impact on adults.

2.8.10 *Trans* fatty acid (TFA)

Trans fatty acid (TFA) is a component of fatty acid present in the human diet. The Food and Drug Administration (FDA) defined TFA as the sum of all unsaturated fatty acids that contain one or more isolated (i.e., non-conjugated) double bond(s) in *trans* configuration [67]. On the other hand, the European Food Safety Authority (EFSA) defined TFA as those fatty acids present as either *trans* - MUFA or *trans* - PUFA. *Trans* PUFAs have at least one *trans* double bond and may therefore also have double bonds in the *cis* configuration. Conjugated fatty acid (CLA) is separated from TFA as an independent section by EFSA. CLAs are thought to have health benefits that are different from those of TFAs, such as anti-cancer [68] and anti-atherosclerosis [69] activities, therefore it is appropriate to exclude CLA from the definition of TFA.

2.8.11 Omega - 6/omega - 3 fatty acid ratio (n-6/n-3 FA ratio)

Omega - 6 and omega - 3 polyunsaturated fatty acids (PUFAs) are essential fatty acids that must be derived from diet since they cannot be produced by humans and other mammals because of the lack of endogenous enzymes for omega - 3 desaturation [70]. As a result of agri-business and modern agriculture, western diets contain excessive levels of omega - 6 PUFAs but very low levels of omega - 3 PUFAs, leading to an unhealthy omega - 6/omega - 3 ratio of 20:1, instead of the 1:1 ratio during evolution in humans [71]. Thus, an unbalanced omega - 6/omega - 3 ratio in favor of omega - 6 PUFAs is highly prothrombotic and proinflammatory, which contributes to the prevalence of atherosclerosis, obesity and diabetes [70, 71, 72]. Regular consumption of diets rich in omega - 3 PUFAs have been associated with low incidence of these diseases, particularly in Icelandic populations, Inuit indigenous people, and Native Americans in Alaska [73, 74].

2.8.12 Peroxidizability index (PI)

The PI was determined according to Du et al. [75]:

$$PI = (\text{monoenoate} \times 0.025) + (\text{dienoate} \times 1) + (\text{trienoate} \times 2) + (\text{tetraenoate} \times 4) + (\text{pentaenoate} \times 6) + (\text{hexaenoate} \times 8) \quad (8)$$

All health indices determinations were in duplicate.

2.8.13 Conversion of crude fat to true - total fatty acid (T - TFA) or edible portion in g/100 g (EP/100g)

Conversion from individual fatty acid (FA) as '% of total fatty acids (FACID)' (= FA as 'g per 100 g FACID') to individual FA as 'g per 100 g EP' (applicable if the FACID content per fat or food is not given).

When the content of total fatty acid in food or fat is not given, it is not necessary to calculate it by using fatty

acid conversion factors (XFA). The conversion factors reflect the ratio between the sum of fatty acid and total lipids (TL) in the food [47].

$$\text{FACID (g/100 g EP)} = \text{TL (g/100 gEP)} \times \text{XFA} \quad (9)$$

Fatty acid conversion factors had earlier been derived for various food products and summarized by Greenfield and Southgate [75]. As fatty acid conversion factors (XN) are given only for lean (0.7) and fatty fish (0.9) (without indication of corresponding fat content) and not for crustaceans and mollusks, FAO/INFOODS [76] made further investigations on these factors. The findings concluded that instead of using fixed factors it is more accurate to use the formula proposed by Weihrauch et al. [47], who also proposed formulas for crustaceans and mollusks. [*Pandalus borealis* is a crustacean.]

Two ways to estimate fatty acid conversion factors are proposed:

If fat is ≥ 0.55 g/100 g EP, the formula of Weihrauch et al. [47] (should be used for crustaceans).

$$\text{Crustaceans: XFA} = 0.956 - 0.237/\text{TL} \quad (10)$$

Note: Total lipids (TL) should be expressed as g/100 g EP.

The EP/100g (T-TFA) values were depicted in Table I.

2.8.14 Energy density values as concerned the T – TFA, CF and other lipids (OLS)

The energy equivalents (kJ/100g and kcal EP/100g) were calculated for CF, T-TFA and OLs in the samples

$$\text{kJ/100 g} = 37.0 \times \text{CF} + \text{T-TFA} + \text{OLS} \quad (11)$$

$$\text{kcal/100 g} = 9.0 \times \text{CF} + \text{T-TFA} + \text{OLS} \quad (12)$$

Other lipids = phospholipids (PHOLIP), cholesterol (CHOLE), etc.

2.9. STATISTICAL ANALYSIS

In the statistical analysis, two models were used: descriptive statistics and inferential statistics [77]. In the descriptive model, values determined were grand mean, standard deviation (SD), and coefficient of variation per cent (CV%). In the inferential model, the following was determined: linear correlation coefficient (rxy), variance or coefficient of determination (rxy²), and linear regression coefficient (Rxy). The rxy was subjected to the standard Table (critical) value at rxy = 0.01 (rC(0.01)) at n-2 (df) to see if significant differences existed in the compared samples. Furthermore, the generated rxy values were used to calculate the coefficient of alienation (CA) and index of forecasting efficiency (IFE).

3. RESULTS AND DISCUSSION

Table I contained the following: contents of crude fat (CF), true-total fatty acid (T-TFA) and other lipids (OL) of the samples. The range of the CF was 0.80 to 1.31 g/100 g with mean of 1.14 ± 0.291 g/100 g and CV% of 25.4; the slightly high CV% was due to the CF in the shell because the value in whole shrimp and flesh (1.31) > whole organism (1.30) > shell (0.80). The CF across the board was relatively low. The corresponding T-TFA (or EP/100g) range was 0.53 to 1.02 g/100 g; after multiplying CF by these conversion factors: whole organism (1.30 x 0.774), flesh (1.31 x 0.775) and shell (0.80 x 0.660). The energy density from the CF, T-TFA and OL levels were relatively low at these values in kJ/100 g and kcal/100g: CF (29.6 - 48.5/7.20-11.8);

Table I – Crude fat (CF), true-total fatty acid (T-TFA), other lipids (OLs) and their corresponding energies of whole organism, flesh and shell (exoskeleton) of *Pandalus borealis* shrimp

Parameter	Whole organism	Flesh	Shell	Mean	Standard deviation (SD)	Coefficient of variation percent (CV%)
Crude fat(CF) (g/100g)	1.30* ¹	1.31* ²	0.80* ³	1.14	0.29	25.4
T-TFA (or EP/100g)	1.01	1.02	0.53	0.85	0.28	32.9
Other lipids (OL) (g/100g)	0.29	0.31	0.27	0.29	0.02	6.90
Energy (in kJ)						
– CF (kJ/100g)	48.1	48.5	29.6	42.1	10.8	25.7
– T-TFA (kJ/100g)	37.2	37.6	19.5	31.4	10.3	32.8
– OL (kJ/100g)	10.9	11.3	10.1	10.8	0.63	5.83
Energy (in kcal)						
– CF (kcal/100g)	11.7	11.8	7.20	10.2	2.62	25.7
– T-TFA (kcal/100g)	9.05	9.14	4.75	7.65	2.51	32.8
– OL (kcal/100g)	2.65	2.75	2.45	2.61	0.15	5.75

*1 = CF x 0.774; *2 = CF x 0.775; *3 = CF x 0.660; EP = edible portion; OL = phospholipids (PHOLIP) and cholesterol (CHOLE)

Table II – Classic fatty acid indices of *Pandalus borealis* shrimp whole organism, flesh and shell (% of total fatty acids)

Index	Whole organism (%)	Flesh (%)	Shell (%)	Mean	SD	CV%
Σ SFA	18.3	18.8	19.6	18.9	0.66	3.49
Σ MUFA	40.0	29.2	40.6	36.6	6.42	17.5
Σ TFA	1.50E-4	9.00E-5	1.00E-4	1.10E-4	3.00E-5	28.4
Σ n-6 PUFA	24.0	23.5	23.1	23.5	4.51E-1	1.92
Σ n-3 PUFA	17.8	18.5	16.7	17.7	9.07E-1	5.12
Σ n-6 + n-3 PUFA	41.8	42.0	39.8	41.2	1.22	2.96
Σ UFA	81.8	71.2	80.4	77.8	5.76	7.40
EPA	8.87	7.16	5.80	7.28	1.54	21.2
DHA	8.88	11.4	10.9	10.4	1.33	12.8

Table III – Relevant saturated fatty acid (SFA) (% of total fatty acid) for this study in the three samples of *Pandalus borealis* shrimp

Saturated fatty acid (SFA)	Whole organism	Flesh	Shell	Mean	SD	CV%
Dodecanoic acid C12:0	0.03	0.05	0.02	0.03	0.02	66.7
Myristic acid C14:0	0.02	0.02	0.01	0.01	0.01	50.0
Palmitic acid C16:0	11.2	10.2	10.3	10.6	0.55	5.20
Stearic acid C18:0	7.01	8.62	9.19	8.28	1.13	13.6
Total	18.3	18.9	19.5	18.9	0.60	3.17

T – TFA or EP/100g (19.5 – 37.6/4.75 – 9.14); OL (10.1 – 11.3/2.45–2.75). The CV% of each series had virtually similar values shown as follows: CF(25.4), CF (kJ/100g) (25.7), CF (kcal/100g) 25.8); T-TFA (32.9), T-TFA (kJ/100 g) (32.8), T-TFA (kcal/100 g) (32.8) and OL (6.90), OL (kJ/100 g) (5.65), OL (kcal/100 g) (5.73). Table II contained the classic fatty acid indices of the samples. The indices were Σ MUFA, Σ TFA, Σ n-6 PUFA, Σ n-3 PUFA, Σ n-6 + Σ n-3 PUFA, Σ UFA, EPA and DHA. For these indices the CV% values were generally low at 1.92 to 28.4%, showing Σ TFA to have the highest CV% (28.4) and Σ n-6 PUFA the lowest CV% (1.92). The Σ SFA amounted to about half of its corresponding Σ MUFA per sample, shown as follows [Σ SFA/ Σ MUFA (%total fatty acid)]: whole organism (18.3/40.0), flesh (18.8/29.2) and shell (19.6/40.6), respectively. There appeared to be parity between Σ SFA/ Σ n-3 PUFA seen as follows: whole organism (18.3/17.8), flesh (18.8/18.5) and shell (19.6/16.7). The Σ SFA values were simply lower than their corresponding Σ n-6 PUFA: whole organism (18.3/24.0), flesh (18.8/23.5) and shell (19.6/23.1). Hence, in all the samples, the following was observed: Σ SFA < Σ n-3 PUFA except (in the shell where we have 19.6/16.7) < Σ n-6 PUFA < Σ MUFA. The Σ TFA values were highly insignificant as they were at ultra-trace levels at 9.00E-5 to 1.5E-4% total fatty acid; this had no dietary significance and is not deleterious in any form. It could be seen that the Σ n-6+n-3 PUFA were high at 39.8 to 42.0% of total fatty acids. These results were nutritionally highly positive. On the whole, the Σ UFA/ Σ SFA showed that total energy density is shared between the samples as follows: Σ SFA: 18.3% to 19.6% energy content (kJ/100g/kcal/100g), whereas Σ UFA exhibits percentage values of 71.2% to 81.8% energy content (kJ/100g/kcal/100g). These energy sources were highly complemented by 5.80% to 8.87% energy (EPA) and 8.88% to 11.4% energy

(DHA). The general low levels of (kJ/100g/kcal/100g) SFA and low energy density in the *Pandalus borealis* were nutritionally advantageous to the consumer. Since every other parameter originated from the CF, the lipid profiles (and their other parameters) followed this trend (g/100g); shell (19.6) > flesh (18.8) > whole organism (18.3), although the values were highly close with a CV% of 3.49.

The SFA values relevant to this study were depicted in Table III. They were dodecanoic acid (C12:0), myristic acid (C14:0), palmitic acid (C16:0), and stearic acid (C18:0). The SFA values were relatively low, but close in values depicted as follows. Total sample values were (%total fatty acid): shell (19.5) > flesh (18.9) > whole organism (18.3) with mean of $18.9 \pm 0.60\%$ and CV% of 3.17. Relatively close values existed in the following SFA pairs in the samples: C12:0/C14:0 (0.02 to 0.05/0.01 to 0.02); and C16:0/C18:0 (10.2 to 11.2/7.01 to 9.19). The percentage values of C16:0, C18:0 and C16:0+C18:0 on the overall sample SFA reading made interesting readings. The C16:0/C18:0 percentage value on the overall SFA per sample showed the following: whole organism (61.4/38.4), flesh (54.0/45.7) and flesh (52.8/47.1); whereas, C16:0+C18:0 overall values over the total SFA values per sample had virtually similar results of whole organisms (99.8%), flesh (99.7%) and shell (99.9%). In this light it could be hypothesized that the nutritional behaviors of the SFAs in the whole organism $\equiv$ flesh $\equiv$ shell. More specifically, however, the following could be concluded in the SFAs of *P. borealis*. SFAs responsible for raising serum cholesterol are C12:0, C14:0 and C16:0, thereby inhibiting the activity of low density lipoprotein receptors (LDLRs); C18:0 appeared to be biologically neutral as it can easily be metabolized to oleic acid and have no effect on circulating LDL-C levels [56]. In these results, the total C12:0 +C14:0 was 0.20% total SFA (whole organism), 0.30%

total SFA (flesh) and 0.10% total SFA (shell); all these were trace values, hence only C16:0 could be nutritionally recognized in the SFA activity in the *P. borealis*. Hence, the pro-atherogenic and the pro-thrombogenic potentials of *P. borealis* oil are very low [58].

Table IV contained the monoenoic fatty acids (% total fatty acids) in the samples. The monoenoic fatty acids ultra-trace levels were myristoleic acid [C14:1 (cis-9)] (2.00E-5 to 3.00E-4%) with CV% of 24.8; and nervonic acid [C24:1 (cis-15)] (2.00E-5 to 2.00E-4%) with CV% of 0.00; trace level was erucic acid [C22:1 (cis-13)] (0.01 to 0.26%) and highest CV% (86.7). Average MUFA values (less than two units) were observed in palmitoleic acid [C16:1 (cis-9)] (3.69 to 4.63%) with low CV% (11.2), petroselinic acid [C18:1 (cis-6)] (5.12 to 6.77%) with low CV% (14.4) and gadoleic acid [C20:1 (cis-11)] (9.99 to 15.9) with CV% (22.7). Arguably, the highest monoenoic fatty acid in the samples was oleic acid [C18:1 (cis-9)] (14.8 to 18.4%) with CV% (11.2, lowest CV% value). However, oleic and gadoleic fatty acids were very close or even similar values, particularly in flesh and shell; see the following comparisons (%) in oleic/gadoleic fatty acids: whole organism (18.4/9.99), flesh (14.8/13.5) and shell (15.9/15.9). The total MUFAs per sample had this close range of 39.2 to 40.6% with the Table IV closest (lowest) CV% (1.75). The high MUFA values specifically contribute to the UFAs that are considered to be anti-atherogenic, as they inhibit the accumulation of plaque and reduce levels of phospholipids, cholesterol and esterified fatty acids [58], while also contributing positively to lowering the thrombogenicity index, which is beneficial for CVH.

Table V presents the *trans* fatty acids. They were exclusively part of the monoenoic fatty acids, but because of their negative nutritional effects, they were separately discussed. The TFAs in *P. borealis* were due to microbial activity within the shrimp and were insignificant to the fatty acids content in the samples. Values were all at ultra-trace levels in the samples (total = 9.00E-5 to 1.50E-4%, $0.1.10E-4 \pm 3.20E-5\%$ and CV% = 28.4). Consumption of *Pandalus borealis* would not cause deleterious effects in its consumers.

In Table VI, dienoic fatty acid profiles were shown. Four fatty acids were exhibited. Two of the fatty acids were in ultra-trace levels and their values were completely insignificant as they ranged as follows: eicosadienoic acid [C20:2 (cis-11, 14)] (2.00E-5 to 3.00E-5%) and rumenic acid [C18:2 (cis-9, trans -12)] (6.00E-5 to 9.00E-5%); they both have a close CV% of 24.8/24.7. Docosadienoic acid [C22:2 (cis-13, 16)] ranged from trace level to low level (0.10 to 0.34%) with highest CV% (88.5). Significant levels were measured in linoleic fatty acid [C18:2 (cis-9, 12)] (18.0 to 19.0%) and lowest CV% (2.88). The total dienoic fatty acids in the samples ranged from 18.2 to 19.3% (of total fatty acid). Of these values, linoleic acid comprised the following percentages: whole organism (98.2%), flesh (99.5%), and shell (95.8%), leaving these values for the other three members of the dienoic fatty acids: 1.80 (whole organism), 0.50 (flesh), and 1.20 (shell). The high dienoic acid values contribute to a low index of atherogenicity (IA), low index of thrombogenicity (IT), high level of hypocholesterolemic/hypercholesterolemic ratio (HH), health-promoting index, unsaturation index, low

Table IV – Monoenoic fatty acid (%total fatty acid) in the whole organism, flesh and shell of the *P. borealis* shrimp samples

Monoenoic fatty acid	Whole organism	Flesh	Shell	Mean	SD	CV%
Myristoleic acid C14:1 (cis-9)	3.00E-5	2.00E-5	2.00E-5	2.33E-5	5.77E-6	24.8
Palmitoleic acid C16:1 (cis-9)	4.63	4.17	3.69	4.16	0.47	11.3
Petroselinic acid C18:1 (cis-6)	6.77	6.45	5.12	6.11	0.88	14.4
Oleic acid C18:1 (cis-9)	18.4	14.8	15.9	16.4	1.85	11.3
Gadoleic acid C20:1 (cis-11)	9.99	13.5	15.9	13.1	2.97	22.7
Erucic acid C22:1 (cis-13)	0.18	0.26	0.01	0.15	0.13	86.7
Nervonic acid C24:1 (cis-15)	2.00E-5	2.00E-5	2.00E-5	2.00E-5	-	-
Total	40.0	39.2	40.6	39.9	0.70	1.75

Table V – Trans fatty acids (part of monoenoic fatty acids) in the three samples of the *P. borealis* shrimp samples

Trans fatty acid	Whole organism	Flesh	Shell	Mean	SD	CV%
Trans – petroselinic acid C18:1 (trans-6)	8.00E-5	5.00E-5	5.00E-5	6.00E-5	1.73E-5	28.8
Elaidic acid C18:1 (trans-9)	7.00E-5	4.00E-5	5.00E-5	5.33E-5	1.53E-5	28.7
Vaccenic acid C18:1 (trans-11)	0.00	0.00	0.00	0.00	-	-
Total	1.50E-5	9.00E-5	1.00E-4	1.13E-4	3.21E-5	28.4

Table VI – Dienoic fatty acids (%total fatty acids) in the samples of *P. borealis* shrimp

Dienoic fatty acid	Whole organism	Flesh	Shell	Mean	SD	CV%
Linoleic acid C18:2(cis-9,12)	19.0	18.2	18.0	18.4	0.53	2.88
Eicosadienoic acid C20:2(cis-11,14)	3.00E-5	2.00E-5	2.00E-5	2.33E-5	5.77E-6	24.8
Docosadienoic acid C22:2(cis-13,16)	0.34	0.10	0.22	0.19	0.17	88.5
Rumenic acid C18:2(trans-9, cis-12)	9.00E-5	6.00E-5	6.00E-5	7.00E-5	1.73E-5	24.7
Total	19.3	18.3	18.2	18.6	0.61	3.28

n-6/n-3 and relatively low PUFA/SFA (which were all nutritionally positive) in *Pandalus borealis*.

The trienoic acid levels in Table VII had four members which were gamma-linoleic acid [C18:3 (cis-6,9,12)], dihomo-gamma-linolenic acid, DGLA [C20:3 (cis-8,11,14)], alpha-linolenic acid [C18:3 (cis-9,12,15)] and eicosatrienoic acid [C20:3 (cis-11,14,17)], but only gamma-linoleic acid had low but relatively significant levels at 0.16 to 0.24%, 0.19±0.04% and CV% (21.1). Gamma-linoleic acid percentages (in the overall levels) were 99.7% (whole organism), 99.6% (flesh), and 98.0% (shell). Trienoics were very active in determining the values of unsaturation index (UI) and the peroxidizability index (PI).

Table VIII contained a member in each of these groups: tetraenoic acid, arachidonic acid [C20:4 (cis-5, 8 11, 14), 4.45 to 5.02%, CV% (6.09)]; pentaenoic acid, EPA [C20:5 (cis-5, 8, 11, 14, 17), 5.80 to 8.87%, CV%(21.2)]; hexaenoic acid, DHA[C22:6 (cis-4,7,10,13,16,19), 8.88 to 11.4%, CV% (12.8)]. All the fatty acids in Table VIII were involved in the calculations for: PUFA/SFA, IA, IT, HH, HPI, UI and n-6/n-3 ratio; EPA and DHA were further involved in the determination of EPAT + DHA and FLQ, whereas only arachidonic acid (ARA, a

tetraenoic) was involved in the calculation of PI.

Statistical analysis of the classic fatty acid indices of *Pandalus borealis* samples (see Table II) were explained in detail, as shown in Table IX. Table IX depicts: r_{xy}, r_{xy}², R_{xy}, mean, SD, CV%, CA and IFE; value of level of significance was also set at r_{xy}=0.01 at n-2(df). The pairs compared were whole body/flesh (W/F), flesh/shell (F/S) and whole organism /shell (W/S). The r_{xy} values were positive, high (0.9856 to 0.9979) and significantly different since all r_{xy} values were each higher than the critical value of 0.798. The r_{xy}² followed the trend observed in the r_{xy} and their values were high at 0.9715 – 0.9958. The R_{xy} values were high at 0.8492 to 1.131. The R_{xy} values deserve further explanation. The R_{xy} could be written as Rx:y or Rx:Ry. Where X represents the left hand member of a pair, as in Table IX, X would be as follows: W(in W/F), F(in F/S) and W(in W/S), whereas y represents letters in the right hand side of a pair: F(in W/F), S(in F/S) and S(in W/S). Values of x were permanent one unit (or 100%) in each R_{xy} value, whereas y could be seen in the Table IX as ranging from 0.8492 to 1.131. This showed that the real expression of R_{xy} would be, taking W/F as an example: R_{xy}= Rx(=1.00): Ry(0.8492). That is, for each 1

Table VII – Trienoic fatty acids (% total fatty acids) in the whole organism, flesh and shell samples of *P. borealis* shrimp samples

Trienoic fatty acid	Whole organism	Flesh	Shell	Mean	SD	CV%
Gamma-linoleic fatty acid C18:3 (cis-6,9,12)	0.24	0.18	0.16	0.19	0.04	21.1
DGLA C20:3 (cis-8,11,14)	4.00E-4	6.00E-4	3.00E-4	4.33E-4	1.53E-4	35.3
Alpha-linolenic acid C18:3 (cis-6,12,15)	1.00E-4	8.00E-5	1.00E-4	1.27E-4	6.43E-5	50.6
Eicosatrienoic acid C20:3 (cis-11, 14,17)	1.00E-4	8.00E-5	9.00E-5	9.00E-5	1.00E-5	7.87
Total	0.24	0.18	0.16	0.19	0.04	21.1

Table VIII – Tetraenoics, pentaenoics and hexaenoics fatty acids (% total fatty acids) in the *P. borealis* samples

Enoic fatty acid	Whole organism	Flesh	Shell	Mean	SD	CV%
<i>Tetraenoic</i>						
Arachidonic acid C20:4 (cis-5,8, 11,14)	4.45	5.02	4.80	4.76	0.29	6.09
<i>Pentaenoic</i>						
EPA C20:5 (cis-5,8,11,14,17)	8.87	7.16	5.80	7.28	1.54	21.2
<i>Hexaenoic</i>						
DHA C22:6 (cis-4,7,10,13,16,19)	8.88	11.4	10.9	10.4	1.33	12.8

Table IX – Statistical analysis of classic fatty acid indices of *Pandalus borealis* samples (whole organism, flesh, shell) [Data from Table II.]

Statistics	Whole body/flesh (W/F)			Flesh/shell (F/S)			Whole body/shell (W/S)		
	Whole body	W/F	Flesh	Flesh		Shell	Whole organism		Shell
r _{xy}		0.9885*		F/S	0.9856*	W/S		0.9979*	
r _{xy} ²		0.9770			0.9715			0.9958	
R _{xy}		0.8492			1.13			0.9841	
Mean	26.8		24.6	24.6		26.3	26.8		26.3
SD	24.9		21.4	21.4		24.5	24.9		24.5
CV%	92.7		86.7	86.7		93.2	92.7		93.2
C _A		0.1517			0.1688			0.0648	
IFE		0.8483			0.8312			0.9352	

r_{xy} = linear correlation coefficient; r_{xy}² = coefficient of determination; R_{xy} = regression coefficient; SD = standard deviation; CV% = coefficient of variation percent; C_A = coefficient of alienation; IFE = index of forecasting efficiency; * = values significantly different at n-2 = 9-2 = 7(df) and r_{xy} critical = 0.798 at r_{xy}=0.01

unit increase in the X value, there was a corresponding increase of 0.8492 in the y value. It could then be written as $R_{xy} (W/F=W(1.00): F(0.8492))$. This scenario holds for other pairs in Table IX. Unlike the r_{xy} , r_{xy2} and R_{xy} that joined a pair as one unit, the mean, SD and CV% had individual readings for each member in a pair group. Three means, three SDs and three CV%s were shown in Table IX, but each of these values appears twice depending on the three pairs of the comparisons. Mean, SD and CV% in W were $26.8 \pm 24.9\%$, CV% (92.7); in F, it was $(24.6 \pm 21.4\%, \text{CV}\% (86.7))$; S was $26.3 \pm 24.5\%$, CV% (93.2), respectively. Mean, SD and CV% values in W were closer to S than F, with all these values being lowest in F. The CA was low in all the pair groups with values ranging from 0.0648 to 0.1688. The CA represents values of non-relationship or alienation within a group. It also represents error of prediction of relationship in a compared relationship. The CA statistical partner is IFE. $CA+IFE=1.00$ (if fraction is the considered model of comparison) or $CA + IFE=100\%$ (if percentage is the model of comparison). IFE represents the reduction of error in the prediction of relationship in a compared entity. Hence, when CA is high, IFE is low or in the reverse situation. In the situation here, since all CA(0.0648-0.1688) values were low, all the corresponding IFE (0.8312 – 0.9352) values were high, or, CA(6.48%-16.88%) $\lll$ IFE (83.12%-93.52%). The high values of IFE showed that high nutrition/biochemical relationships existed in the pairs of W/F, F/S and W/S. Furthermore, due to the high IFE values, it followed that the member of a pair could carry out all the food properties of the other member of the group and vice-versa. [Note that CA and IFE treated a pair as a unit, just as occurred in r_{xy} , r_{xy2} and R_{xy} .]

3.1. LIPID SAMPLES' NUTRITIONAL INDICES WERE SHOWN IN TABLE X

The index of atherogenicity (IA) values in the samples were low at 0.13 to 0.14 and CV% of 13.3. These values were mostly lower than many literature results. Yurchenko et al. [59] concluded that consumption of food or products with a low IA can reduce the levels of total cholesterol and LDL-C in human blood plasma. Nantapo et al. [78] analyzed fatty acid consumption of milk at different stages of lactation, finding IA to range from 4.08 to 5.13 in different lactation stages. Akintola [79] investigated the techniques of smoking and sun drying to assess the nutritional quality of southern pink shrimp (*Penaeus notialis*), reporting IA values of 0.71 to 0.82. Seaweeds range from 0.03 to 3.58 [80], crops from 0.08 to 0.55 [81], fish from 0.21 to 1.41 [82], meat from 0.17 to 1.32, and dairy products from 1.42 to 5.13 [83, 78]. The Eskimo diet has an AI value of 0.39. The index of thrombogenicity (IT) in Table X had values ranging from 0.21 to 0.24 and CV% value of 8.70; these values were also low, as in AI. TI value in the Eskimo diet is 0.28 (higher than in the present report).

Foods or products with low IT are beneficial for CVH [84]. Chen et al. [85] conducted a comparative study on the fatty acid profiles of four different Chinese medicinal *Sargassum* seaweeds; results showed IT was between 0.46 and 1.60. Calabrò et al. [81] worked on fatty acid profiles of three cultivars of *Lupinus albus* (Lutteur, Lublanca, Multitalia). Further literature on IT shows seaweeds had values ranging from 0.04 to 2.94 (except *Gracilaria salicornia*, which had an IT value of 5.75) [80]. IT values for crops, fish, meat, and dairy products are 0.14-0.56 [81, 86], 0.14-0.87 [87], 0.29-1.69 [88] and 0.39-5.04 [83, 89], respectively. Any fatty acid composition with a low IT has a better nutritional quality and its consumption may reduce the risk of coronary heart disease (CHD) [84].

The hypocholesterolemic/hypercholesterolemic (HH) ratio values in Table X range from 5.35 to 5.53. Paiva et al. [90] worked on the fatty acids in selected four Azorean macroalgae and found the HH values to range from 1.26 to 2.09. Ratusz et al. [91] analyzed fatty acids content in 29 cold-pressed camelina (*Camelina sativa*) oils and found relatively high HH that ranged from 11.7 to 14.7. For shellfish, HH value ranges from 1.73 to 4.75 (except for *Loxechinus albus*, 0.21) [92]; for fish, value ranges from 1.54 to 4.83 (except *Opisthonema oglinum*, 0.87) [93]. For meat and dairy products, ranges are from 1.27 to 2.79 [94, 88] and 0.32 to 1.29 [95, 83], respectively.

Health-promoting index (HPI) levels in the samples, as shown in Table X, showed range values of 6.90 to 7.76, with low CV% (5.89). HPI is the reverse of AI. Literature on dairy products had an HPI range of 0.16 to 0.68. Dairy products with high HPI values are assumed to be more beneficial to human health [84]; this might be true for *Pandalus borealis* oil.

Unsaturation index (UI) values in the samples ranged from 154 to 162 (Table X). Colombo et al. [96] used UI to compare macroalgae in cold water with those in warm water, with a high UI value that indicates a high degree of total unsaturation. Their results suggested that the fatty acids with a high level of unsaturation in a membrane lipid can maintain fluidity at a relatively low temperature. The UI values of seaweeds vary from 45 to 369 [97], which may likely be related to their species; the range for meat is 73 ± 6 to 124 [98, 99], while for dairy products the range is 86-120 [100].

EPA + DHA is an index that is recognized worldwide. The FAO of the United Nations (UNFAO) [84] recommended amount is 0.250-2g/day. This index is mostly used to evaluate the nutritional quality of seafood and its products, particularly fish. The EPA + DHA values reported in Table X were in percentage and mg/100 g. Sample values were: whole organism (17.8% or 179 mg/100 g), flesh (18.6% or 188 mg/100 g) and shell (16.7%, 88.2mg/100g). Rincón-Cervera et al. [92] studied the fatty acid composition of fish and shellfish captured in South Pacific. The results showed that

EPA + DHA ranged between 115 and 137 mg/100 g in all studied fish species and between 63.6 and 523 mg/100 g in all studied shellfish species.

The fish lipid quality/flesh lipid quality (FLQ) in the samples ranged between 13.4 and 24.3 (Table X). Marine products have higher proportions of EPA and DHA; hence, this index may be more appropriate for them [84]. Literature reports on fatty acid profiles of the fillet of farmed sea beam (*Sparus aurata*) harvested in different seasons found FLQ to be lowest in April. FLQ values in fish varies between 13.0 to 36.4 [66] (for closely related species); present results were highly comparable to these literature results.

The linoleic acid/ α -linolenic acid (LA/ALA) ratio values were not shown in Table X. The paired values of LA/ALA are demonstrated as follows (in percentages): whole organism (19.0/.2.00E-4), flesh (18.2/0.8.00E-5), and shell (18.0/1.00E-4). These values resulted in these ratios of LA/ALA: whole organism (95,000:1.00), flesh (227, 500:1.00) and shell (180,000:1.00). C20:4n-6, cis values were each less than one-third of their corresponding LA depicting values of 4.45-5.02% and in the n-3 PUFA, both C20: 5n-3 and C22:6n-3 were already preformed in the samples, as already depicted in the relevant tables. Hence, while LA might exhibit essentiality in the present result, ALA was virtually non-essential. The Definitions and Nutrient Composition Section of the Guidelines for Infant Formula published by Food Standards Australia New Zealand (FSANZ) sets the minimum and maximum proportions of LA and ALA, specifying an LA/ALA ratio within 5:1 - 15:1 [84].

The n-6/ n-3 values in Table X showed the range as 1.27 to 1.38 and CV% of 4.51. Recent dietary guidelines are focused on n-6 and n-3 PUFA balance. The recommendations of Bellagio's report on healthy agriculture, healthy nutrition, and healthy people indicated that a ratio (4:1) of n-6 PUFA to n-3 PUFA in the diet should be the goal [101]. A balance existed between omega-6 and omega-3 fatty acids during the long

evolutionary history of the genus Homo [102]. During evolution, omega-3 fatty acids were found in all consumed foods: particularly meat, fish, wild plants, nuts, and berries [102, 103]. A diet rich in omega-6 fatty acids shifts the physiological state to one that is proinflammatory, prothrombotic, and proaggregatory, with increases in blood viscosity, vasospasm, vasoconstriction, and cell proliferation [104].

Trans fatty acids (TFAs) were present in ultra-traces (9.00E-5% to 1.50E-4%) in the samples as shown in Table X. According to population nutrient intake figures from the WHO/FAO, the intake of TFA should constitute < 1% of total energy. For pregnancy and lactation, the lowest possible intake of industrially-produced TFAs is required [84]. According to the EFSA, TFA in the diet is provided by several sources that contain EFAs and other nutrients [105]. The EFSA panel concluded that the intake of TFA should be sufficiently reduced within a nutritionally adequate diet to lower the intake of TFA, while ensuring the nutrient intake [105]. The 2015-2020 Dietary Guidelines for Americans emphasize that individuals should reduce their intake of *trans fatty acid* to as low as possible by limiting their consumption of foods that contain synthetic sources of *trans fats* [84]. There may be no need to eliminate meat and dairy products that contain small quantities of natural TFA from the diet. In the United Kingdom, the recommended intake of TFA is < 2% of the total daily energy or 5 g/day [84]. The TFA index is presently used in seaweed [90], lamb [106], milk [95], fish [107], and plant oil [108]. Skalecki et al. [107] reported similar values of TFA in Prussian carp fish (*Carassius gibelio*) filets with and without skin; TFA values were 1.06%±0.06%, 10.6-37.2 mg/100 g. The present TFA values were 9.00E-5% - 1.50E-4%, 7.00E-5 mg/100 g - 1.20E-4 mg/100 g, which were all less than in Prussian carp fish.

The peroxidizability index (PI) values in Table X ranged from 161-174 with a mean±SD of 166±7.00 and CV% of 4.22. The highest and lowest PI was estimated in

Table X – Sample lipids nutritional indices in *Pandalus borealis* samples (whole organism, flesh, shell)

Indices	Whole organism	Flesh	Shell	Mean	SD	CV%
AI	0.1380	0.1449	0.1288	0.1372	0.0081	5.904
TI	0.2116	0.2280	0.2359	0.2252	0.0124	5.506
HH	5.354	5.534	5.393	5.427	0.0947	1.745
HPI	7.246	6.901	7.762	7.303	0.4333	5.933
UI	157.7	162.3	153.7	157.9	4.303	2.725
EPA+DHA	17.75% 178.6mg/100g	18.56% 188.4mg/100g	16.70% 88.18mg/100g	17.67% 151.7mg/100g	0.9326 55.25	5.278 36.42
FLQ	23.07	24.31	13.36	20.25	5.996	29.61
n-6/n-3	1.348	1.270	1.383	1.334	0.0578	4.333
TFA	0.00015% .0012mg/100g	0.00009% 0.00007 mg/100g	0.0001% 0.0007 mg/100g	0.00011 0.00066 mg/100g	0.00003 0.00057	27.27 86.36
PI	38.63	39.73	38.75	39.04	0.6034	1.546
PUFA/SFA	2.284	2.234	2.031	2.183	0.1340	6.138

AI = atherogenicity index; TI = thrombogenicity index; HH = hypocholesterolemic/ hypercholesterolemic ratio; HPI = health-promoting index; UI = unsaturation index; EPA+DHA = sum of eicosapentaenoic acid and eicosahexaenoic acid; FLQ = fish lipid quality/flesh lipid quality; TFA = *trans fatty acid*; PI = peroxidizability index; PUFA/SFA = polyunsaturated fatty acid/saturated fatty acid ratio.

flax (129.09 ± 0.59) and hemp (99.05 ± 0.42) seeds, respectively [109]. In the PI index by Kang et al [110], the most favorable to reduce the risk of CVD is 80-90. It is well-known that PUFAs and particularly ALA are highly susceptible to oxidation [111], which increases the risk of oil deterioration. The ALA values in these results were of no nutritional consequence. Some literature PI values are: coconut (2), tallow (5), palm (12), olive (13), lard (15), poultry (23), canola (40), sunflower (41), corn (57), soybean (65), flaxseed (120), menhaden (214), and algae (258) [112]. Present values were within the value of 120-214.

The PUFA/SFA ratio values in Table X ranged between 2.03 and 2.28. With the aim of lowering serum cholesterol, nutrition recommendations suggested reducing levels of SFA and replacing them with PUFA in the diet [113, 110]. The target for the ratio of PUFA to SFA is 0.4 or above [101]. Other authors reported that a high PUFA/SFA ratio diet enhances oxidative stress because PUFA (particularly ALA) are highly susceptible to lipid peroxidation. They also indicated that a PUFA/SFA ratio of 1.0-1.5 and a PI value of 80-90 in the diet are within a favorable range to reduce the risk of CVD [109]. PUFA/SFA in the literature are: seaweed (0.42-2.12) [80], except for *Gracilaria changii* (6.96 ± 0.98) [97]; meat (0.11-2.04), fish (0.50-1.79), shellfish (0.20-2.10) and dietary products (0.20-0.18) [80]. PUFA/SFA of chicken is in the range of 0.31-2.04 for different dietary treatments [89]. Fernandes et al. [94] on their report for PUFA/SFA in four species of Brazilian fish had values of 1.09-1.47.

CONCLUSIONS

In line with consumer interest, this study was based on body parts of *Pandalus borealis* (whole organism, flesh and shell), depicting their crude fat (CF), total-true fatty acids (T-TFAs), corresponding energy values, classic fatty acid indices, and nutritional quality indices. Among the classic fatty acid indices, the following were observed: CF was low, other lipids were low, edible fatty (T-TFAs) acids were low, and energy density was low; percentage levels of Σ SFA (low), Σ MUFA (high), Σ TFA (ultra-trace), Σ n-6 + n-3 PUFA/ Σ UFA (high), EPA and DHA (reasonably advantageous nutritionally). Significant differences existed in the compared pairs of the classic fatty acid values: whole organism/flesh (W/F), flesh/shell (FS), and whole organism/shell (W/S); with high IFE, thereby making food properties interchangeable between pairs. The nutritional quality indices showed the samples' oil to be nutritionally good for favorable health reasons. These were as follows: low AI, low TI, high HH, high HPI, high UI, average levels of EPA +DHA and FLQ, low level of n-6/n-3, insignificant ultra-trace TFA, PI highly comparable to literature values and > 0.4 value in PUFA/SFA. In particular, AI

and TI were better than in the Eskimo diet. The LA/ALA ratios were very poor and foods high in ALA would be required to adjust to low levels in the LA/ALA ratio values. On the whole, the oil in *Pandalus borealis* is good for human consumption.

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Effect of thermal pre-treatment methods on the chemical composition of grape seed oil: a comparative study

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Although grape seed waste is increasingly valorized through oil extraction and biomass use, it still remains underused in several Mediterranean regions, such as Tunisia, where inadequate management may still pose environmental challenges. Valorization of grape seed waste through oil extraction offers a sustainable solution, turning by-products into valuable resources. In this study, the influence of thermal pre-treatment of grape seeds by microwave radiation for 4 min was investigated in comparison with roasting pretreatment at 120°C for 1 h before oil extraction. Thermal treatment improved the grape seed oil (GSO) yield, which amounted to 13.01% after the roasting pretreatment and 11.72% after the microwave pretreatment as compared to the control (10.35%). GC analysis of GSO showed that the fatty acid composition was modified after thermal pretreatment and the predominant fatty acids were palmitic acid, oleic acid, and linoleic acid. The main tocochromanols were γ -tocotrienol (9.46 mg/100 g oil) and α -tocopherol (4.62 mg/100 g oil). β -sitosterol was the major sterol identified in GSO and reached 1.16 mg/g after grape seed treatment with microwaves. The oxidative stability of extracted oils was investigated at different temperatures (90, 100, 110, and 120°C). Results revealed that oxidative stability prolongation from 18.19h up to 20.94h was observed at 90°C after the microwave pretreatment of grape seeds in comparison with non-treated grape seeds. The findings of this research indicated that microwave pretreatment can emerge as a promising strategy to enhance the nutraceutical content of oil extracted from grape seeds.

Keywords: grape seed oil, polyunsaturated fatty acids, oxidative stability, Rancimat test,

1. INTRODUCTION

Grape products involve the creation of large quantities of by-products, which mostly consist of organic waste, water waste, emission of greenhouse gases, and inorganic residues [1]. The researchers decided to evaluate the composition and bioactive molecules of these agro-industrial by-products [2].

Grape seeds can yield up to 22% oil, varying based on the grape variety, the maturation degree of the seeds, the environmental conditions during ripening, and the method of extraction [3]. This oil, characterized by its high content of unsaturated fatty acids, particularly linoleic and oleic acids, along with vitamin E and sterols [4], is gaining popularity in the market. Vitamin E, or tocochromanols, is classified into two main classes, tocopherols and tocotrienols, comprising eight naturally occurring isoforms [5]. Sterols play a vital role in reinforcing cell membranes and regulating biological processes [6]. Collectively, these bioactive compounds exhibit various health benefits, including lowering blood cholesterol [7], reducing cardiovascular risk [8], and exerting anti-inflammatory activity. It is worth noting that excessive intake of linoleic acid, especially in diets with low ω -3 intake, may promote inflammatory responses through the

synthesis of pro-inflammatory eicosanoids. Therefore, the health effects of linoleic acid depend on the overall dietary ω -6/ ω -3 balance [9]. Numerous studies have shown that grape seed oil (GSO) has health-promoting properties, particularly highlighted in *in vitro* studies, demonstrating antioxidant, anti-inflammatory, cardiovascular protective, antimicrobial, and anti-proliferative effects against human colon cancer. These effects may involve interactions with cellular and molecular pathways [10,11]. This research indicated that GSO consumption reduced inflammation and insulin resistance in overweight and/or obese women, likely due to its tocotrienols and phenolic compounds. Additionally, grape seed extracts were found to significantly lower cholesterol levels [12]. Its application as an edible oil has also been recommended due to its appealing sensory qualities. Grape seed oil has been reported to exhibit pleasant sensory characteristics, mainly attributed to its volatile compound profile. Volatile compounds (alcohols, esters, aldehydes, terpenes, ketones ...) such as ethylacetate, hexanal, trans-2-hexanal, trans-2-heptenal, linalool and 3methylbutanol have been identified as major contributors to the fruity, slightly nutty, and fresh aroma of the oil, depending on grape variety and extraction method [13,14]. Tocopherols, unsaturated fatty acids, phytosterols and phenolic compounds (e.g., quercetin, procyanidins, and carotenoids) contribute to its nutritional and oxidative stability [15].

Recently, pretreatment methods for seeds have gained considerable interest in various sectors such as food, nutraceuticals, pharmaceuticals, and cosmetics, due to the enhanced quality of the resulting products [16]. Several pretreatment technologies have been employed, including enzymatic digestion, ultrasonication, microwaving, and roasting. Microwave treatment alters the seed structure, leading to improved oil extraction. Microscopic analyses of microwave-treated rapeseed (*Brassica napus* L.) have shown structural changes in the lipoprotein membranes surrounding lipid bodies, facilitating oil movement through the cell membranes and enhancing extraction efficiency [17]. Given the growing importance of environmental sustainability in agro-industrial practices, further research on integrating grape seed oil extraction and bioactive compound recovery with sustainable methods is needed to address the challenges of waste management and resource use in the Euro-Med region [18]. This study aimed to investigate the impact of grape seed pretreatment on oil quality, focusing on the fatty acid profile, phytosterol, tocopherol, and tocotrienol levels, while also assessing the oil's oxidative stability at temperatures ranging from 90°C to 120°C. Additionally, the kinetic parameters of the oils were examined post-Rancimat testing. To our knowledge, this is the first study to apply and compare these pretreatment methods for grape seeds cultivated in Tunisia.

2. EXPERIMENTAL

2.1. SAMPLE

Grape (*Vitis vinifera* L.var. Carignan) seeds were provided from a wine company in Tunisia and separated by hand picking from foreign materials before pretreatments and oil extraction.

2.2. MICROWAVE PRETREATMENT

The microwave pretreatment was performed in a microwave oven (Model: Panasonic, 800 W, 2450 Mhz). 300 g of whole seeds were placed in a Pyrex petri dish for 4 min with stirring every 1 min. A seed sample with no pretreatment was used as a control.

2.3. ROASTING PRETREATMENT

300 g of whole grape seeds were spread out on a stainless steel plate tightly covered with aluminum foil and heated for 1 h at 120°C in the oven with ventilation (SLW 115 SIMPLE, pol-eko-aparatura, 2500W) with stirring every 15 min. Seeds were cooled to a temperature of 25°C prior to oil extraction.

2.4. OIL EXTRACTION AND PHYTOCHEMICAL ANALYSIS

Oil extraction was performed following the method of Fathi-Achachlouei et al., [19]. The pretreated grape seeds were ground into powder with a steel grinder and 100 g of powder was mixed with 300 ml of hexane in an Erlenmeyer flask on a shaker for 1 h at room temperature. The obtained mixture was filtered and hexane was evaporated using a rotary evaporator (R210, Buchi, Germany) at 55-60°C. Additionally, the oils after evaporation were purged with nitrogen.

Fatty acid methyl esters (FAMES) were used to identify fatty acids of the extracted oils [20] (Harbeoui et al., 2018). 0.1 g of grape seed oil obtained under the different pretreatment conditions was mixed with 2 mL of hexane and 1 mL of methanolic potassium hydroxide (KOH) (0.5M). After 1 min of mixing, 1 mL of the upper phase (hexane phase) was transferred to 2 mL capacity vials. The oil composition analysis was performed by gas chromatography using a Thermo Scientific Trace 1300 gas chromatograph equipped with a flame ionization detector (FID), with a split injector (120:1) operating at a temperature of 285°C with a capillary column (SGE BPX70 60 m × 0.25 mm × 0.22 μ m) and the programming conditions were as follows: initial temperature of the oven was 100°C for 4 min, raised to 240°C at a rate of 3°C/min and ending at 240°C for 10 min. The carrier gas was helium used at a flow rate of 40 mL/min. The fatty acids were compared to their retention times with those of the authentic standard mixture of 37 FAME methyl esters from Restek. Esterification and injection (0.8 μ L) were performed in triplicate.

To determine tocochromanols, the method of Siger et al., [21] was used. 200 mg of oil was dissolved in 10 ml of n-hexane. Separation was then performed using a Waters HPLC system (Waters, Milford, MA, USA) coupled with a fluorescence detector (FLD) detector (Waters 474), a PDA detector (Waters 2998), and a LiChrosorb Si 60 column (250 × 4.6 mm, 5 µm, Merck Millipore, Darmstadt, Germany). The mobile phase was a mixture of n-hexane with 1,4-dioxane (96:4 v/v) at a flow rate of 1.0 mL/min. The quantification of tocochromanols was conducted using data from the FLD with excitation/emission wavelengths of 295/330 nm, respectively. The determination was carried out in duplicate for each sample.

Phytosterols were analyzed according to the method defined by Raczyk et al. [22]. Briefly, oil samples (50 mg) with the internal standard (5α-cholestane, 50 µL) were saponified with 1M KOH in methanol, at room temperature, for 18 h. The unsaponifiable fraction was extracted three times with hexane/methyl tetr-butyl ether (1:1, v/v) and after the solvent was evaporated under nitrogen. Sterols were silylated with sylon BTZ and piridyne (Sigma-Aldrich, St. Louis, MO, USA) and analyzed in an Agilent 7820A GC (Agilent Technologies, Wilmington, DE, USA) equipped with a DB-35MS (Agilent Technologies) capillary column (30 m, 0.20 mm, and 0.33 µm). Analysis parameters were as follows: the oven temperature was initially 100°C, held 5 min, and increased to 250°C at 25°C/min., and to 290°C at 3°C/min; injector and flame ionization detector (FID) temperature was 250°C; carrier gas, helium at 1 mL/min. Phytosterols were identified by comparison of their retention times (relative to 5α-cholestane) with commercially available standards. The determination was carried out in duplicate for each oil.

2.5. RANCIMAT TEST

A Rancimat test was used to determine the oxidative stability of oils and fats under accelerated conditions based on the induction of oxidation of a sample by exposure to high temperatures and continuous air-flow. This causes oxidation of the oil, releasing volatile compounds. The time can be measured by taking a sample and allowing it to completely oxidize and become rancid [20]. Oxidative stability of the oils was determined using a Rancimat 743 Metrohm apparatus (Herisau, Switzerland). The Rancimat test was conducted using samples of 3 g oil that were oxidized at four different temperatures: 90°C, 100°C, 110°C and 120°C, at a constant air flow of 20 L/h. The volatile products formed from the oxidation reaction were soluble in 0.06 L of deionized water. The kinetic analysis was determined following the method of Farhoosh and Seyedeh-zohreh [23].

3. RESULTS AND DISCUSSION

3.1. GRAPE SEED OIL YIELD

Oil yield is a crucial metric for evaluating oilseeds. As illustrated in Figure 1, thermal pretreatments significantly influenced the oil yield. Specifically, the yield of grape seed oil (GSO) increased to 13.01% following microwave treatment and 11.72% after roasting treatment, compared to a control yield of 10.35%. Habeoui et al. [20] noted that oil content in Tunisian grape seeds varied between 6.31% and 12.70%, depending on the variety and environmental conditions. Romanian GSO yield varied between 11.67% and 12.52% [24] while Vietnamese GSO yield was 16.60% [3].

Several factors also impact oil content, including temperature, pressure, extraction time, solvent type, and the extraction method used [25]. Oomah et al. [26] observed that 5 min of microwave treatment increased GSO yield to 15.3%, while a 24-min treatment yielded 15.4%, both exceeding the control yield of 14.6%. Similarly, Lee et al. [27] reported a progressive increase in GSO yield, achieving a 6% increase with 10 minutes of microwave heating and a 5% increase with 5 min of heat treatment compared to the control. These results suggested that dry heat may enhance oil release from the seeds.

3.2. FATTY ACID ANALYSIS

Table I highlights the primary fatty acids present in grape seed oil (GSO), including linoleic acid, oleic acid, palmitic acid, and stearic acid. GSO was characterized by a high proportion of unsaturated fatty acids (UFA) and a low proportion of saturated fatty acids. In untreated GSO, monounsaturated fatty

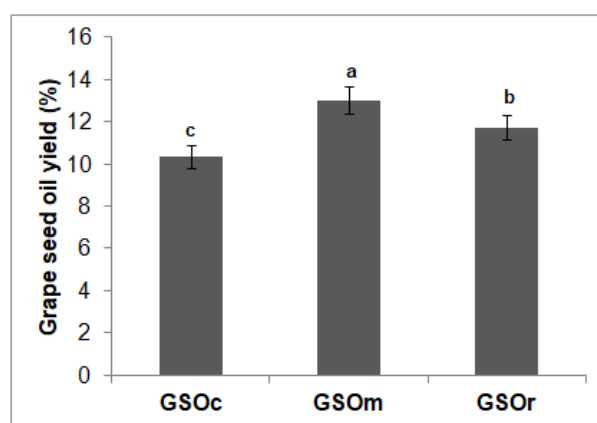


Figure 1 - Grape seed oil yields before and after pretreatments.

GSOc: grape seed oil control; GSOm: grape seed oil after microwave pretreatment; GSOor: grape seed oil after roasting pretreatment.

The small letters (a–c) indicated significant differences ($p < 0.05$) between GSOc, GSOm and GSOor, respectively.

acids (MUFA) comprised 20.78%, while polyunsaturated fatty acids (PUFA) reached 66.86%. The findings of the present study aligned with previous studies on the fatty acid composition of untreated GSO, known to be rich in linoleic acid, containing 61-75%, [3,19,23,15]. Linoleic acid is widely recognized for its beneficial effects on cardiovascular health particularly through its ability to reduce cholesterol levels [28]. However, grape seed oil contained minimal linolenic acid (<1%), which differentiated it from other oils like Nigella seed oil, containing higher linolenic acid levels that can negatively affect oil stability, leading to shorter shelf life due to its susceptibility to oxidation [29]. Fats can be influenced by the variety of the plant, the cultivation environment, and the extraction methods [15].

Chromatography analysis revealed changes in the fatty acid profile following microwave and roasting pretreatments (Table I). After these treatments, the proportions of saturated fatty acids (SFA) slightly increased, while significant alterations were observed in MUFA and PUFA levels – 28.06% and 27.62% for

MUFA, and 59.36% and 60.20% for PUFA, respectively, compared to untreated GSO. The reduction in PUFA proportions was likely linked to the heating temperature and the thermal effects of microwave treatment.

It is important to note that while the profile indicated a decrease in specific acids, an increase in proportion does not necessarily equate to an increase in total content. Therefore, the rise in the proportion of SFA and MUFA mainly resulted from the decline in polyunsaturated acid content.

Theoretically, heat treatment should reduce oil viscosity and facilitate fatty acid release. However, studies by Lee et al. [26] and Pardo et al. [30] found that GSO fatty acid composition remained unchanged after various heat treatments. Similarly, Suri et al. [31] reported a slight increase (1.19%) in SFA content in linseed oil from microwave-treated seeds, alongside minor decreases in MUFA (0.31%) and PUFA (0.87%). Ahmed et al. [32] reported a notable reduction in the levels of polyunsaturated fatty acids (PUFAs), specifically linolenic acid, in sesame oil when roasted at 220°C for 30 min. However, the concentrations of saturated fatty acids (SFAs) and other unsaturated fatty acids remained relatively unchanged.

The stability of the fatty acid composition can likely be explained by the high processing temperatures, which surpassed the melting points of saturated and unsaturated oils. The reduction in specific unsaturated fatty acids may be due to the increase in saturated fatty acids and the breakdown of unsaturated fatty acids during prolonged heating [33].

3.3. TOCOCROMANOL ANALYSIS

Table II presents significant differences in tocochromanol content between treated and untreated Grape Seed Oil (GSO) samples. The main tocochromanols identified were γ -tocotrienol (γ -T3), α -tocotrienol (α -T3), and α -tocopherol (α -T), with concentrations ranging from 6.55 to 9.46 mg/100 g, 5.28 to 8.10 mg/100 g, and 2.08 to 4.62 mg/100 g, respectively. These findings align with Irandoost et al. [10], who reported that GSO has a notably high concentration of tocotrienols, particularly α - and γ -tocotrienol, compared to other vegetable oils.

HPLC analysis revealed that total tocochromanol content in GSO was significantly influenced by the type of pretreatment applied. After roasting, the total tocol content increased to 18.10 mg/100 g, while microwave pretreatment resulted in an even higher total of 24.82 mg/100 g, compared to the control GSO (15.59 mg/100 g). Notably, microwave pretreatment led to a 59.40% increase in total tocochromanols. Additionally, the content of PC-8 rose from 0.24 mg/100 g in the control to 0.47 mg/100 g in the oil extracted after microwave treatment.

Both roasting and microwave pretreatments

Table I - Fatty acid composition of extracted grape seed oils before and after pretreatments

Fatty acid (%)	Grape seed oil		
	GSOc	GSOm	GSO r
C14:0	-	0.04 ± 0.01 ^a	0.04 ± 0.01 ^a
C16:0	6.78 ± 0.21 ^a	5.33 ± 0.12 ^b	5.68 ± 0.15 ^b
C16:1	0.14 ± 0.01 ^b	0.25 ± 0.05 ^a	0.23 ± 0.04 ^a
C18:0	4.57 ± 0.12 ^b	5.44 ± 0.36 ^a	4.96 ± 0.29 ^b
C18:1	20.24 ± 0.56 ^b	27.43 ± 0.85 ^a	27.09 ± 0.98 ^a
C18:2	66.25 ± 1.26 ^a	58.85 ± 1.56 ^b	59.52 ± 1.87 ^b
C18:3	0.34 ± 0.05 ^a	0.25 ± 0.05 ^b	0.24 ± 0.03 ^b
C20:0	0.41 ± 0.06 ^c	0.58 ± 0.07 ^a	0.49 ± 0.06 ^b
C20:1	0.40 ± 0.09 ^a	0.26 ± 0.02 ^b	0.18 ± 0.01 ^c
C22:0	-	0.57 ± 0.08 ^a	0.54 ± 0.09 ^a
C22:1	-	0.12 ± 0.01 ^a	0.12 ± 0.02 ^a
C22:5	0.27 ± 0.02 ^b	0.26 ± 0.01 ^b	0.44 ± 0.02 ^a
C23:0	-	0.12 ± 0.01 ^a	0.11 ± 0.01 ^a
C24:0	-	0.46 ± 0.03 ^a	0.37 ± 0.02 ^b
ΣSFA	11.76 ± 0.33 ^c	12.54 ± 0.11 ^a	12.19 ± 0.72 ^b
ΣMUFA	20.78 ± 0.99 ^c	28.06 ± 0.52 ^a	27.62 ± 0.31 ^b
ΣPUFA	66.86 ± 1.03 ^a	59.36 ± 0.93 ^c	60.20 ± 1.12 ^b

Values are expressed as % of fatty acids (mean ± SD, n = 3). Minor fatty acids (< 0.05%) are not listed; Means within the same row followed by different letters (a,b,c) were significantly different at $p < 0.05$ using Turkey test.

GSOc: grape seed oil control, GSOm: grape seed oil after microwave pretreatment, GSO r: grape seed oil after roasting pretreatment

SFA: saturated fatty acids; MUFA: monounsaturated fatty acids; PUFA: polyunsaturated fatty acids

significantly enhanced ($p < 0.05$) the levels of tocopherols and tocotrienols. These results suggested that thermal pretreatment ruptures cellular structures, facilitating the release of tocopherols and subsequently increasing their concentrations in the extracted oil. This study is the first to report the contents of tocopherols and PC-8 in oils extracted from treated grape seeds using microwave and roasting pretreatments.

Harbeoui et al. [19] examined total tocopherol content in nine Tunisian GSO varieties, finding values between 1.389 and 18.135 mg/100 g oil. Dimić et al. [11] investigated the effect of extraction techniques on tocopherol content in GSO, reporting a maximum of 7.96 mg/100 g oil via microwave-assisted extraction. These findings suggested that GSO was a valuable

source of natural liposoluble antioxidants, offering potential health benefits [11].

3.4. STEROL ANALYSIS

Table III details the sterol content in oils from treated and untreated grape seeds. The primary sterols identified include campesterol, stigmasterol, β -sitosterol, sitostanol, $\Delta 5$ -avenasterol, $\Delta 7$ -avenasterol, and 24-methylenecycloartanol. Total phytosterol contents were measured at 1.40 mg/g for untreated GSO, and 1.81 mg/g and 1.61 mg/g for GSO subjected to microwave and roasting pretreatments, respectively. Notably, β -sitosterol was the predominant phytosterol, reaching 1.16 mg/g after microwave treatment, indicating that this pretreatment enhances phytosterol levels.

Table II - Tocochromanol and Plastochromanol-8 contents of extracted grape seed oils before and after pretreatments

Compound (mg/100g oil)	Grape seed oil		
	GSOc	GSOm	GSO r
α -Tocopherol	2.08 ± 0.05^c	4.62 ± 0.05^a	2.50 ± 0.07^b
β -Tocopherol	0.05 ± 0.01^b	0.21 ± 0.01^a	0.04 ± 0.01^b
γ -Tocopherol	0.95 ± 0.02^c	1.47 ± 0.01^a	1.09 ± 0.04^b
δ -Tocopherol	0.05 ± 0.01^b	0.10 ± 0.01^a	0.06 ± 0.01^b
α -Tocotrienol	5.28 ± 0.04^c	8.10 ± 0.01^a	6.14 ± 0.1^b
β -Tocotrienol	0.15 ± 0.01^b	0.25 ± 0.01^a	0.23 ± 0.04^a
γ -Tocotrienol	6.55 ± 0.08^c	9.46 ± 0.04^a	7.55 ± 0.08^b
δ -Tocotrienol	0.48 ± 0.01^b	0.61 ± 0.06^a	0.49 ± 0.03^b
Total	15.59 ± 0.09^c	24.82 ± 0.12^a	18.10 ± 0.20^b
Plastochromanol-8	0.24 ± 0.01^c	0.47 ± 0.02^a	0.31 ± 0.01^b

All values are means of two repetitions with standard deviation

Means within the same row followed by different letters (a,b,c) were significantly different at $p < 0.05$

GSOc: grape seed oil control, GSOm: grape seed oil after microwave pretreatment, GSO r: grape seed oil after roasting pretreatment

Table III - Phytosterols content of extracted grape seed oils before and after pretreatments

Sterols (mg/g)	Grape seed oil		
	GSOc	GSOm	GSO r
Campesterol	0.13 ± 0.02^c	0.17 ± 0.01^a	0.16 ± 0.01^{ab}
Stigmasterol	0.17 ± 0.01^c	0.20 ± 0.01^a	0.18 ± 0.02^b
β -Sitosterol	0.91 ± 0.06^c	1.16 ± 0.03^a	1.05 ± 0.03^b
Sitostanol	0.05 ± 0.01^{bc}	0.08 ± 0.02^a	0.06 ± 0.01^b
$\Delta 5$ -Avenasterol	0.04 ± 0.01^{bc}	0.06 ± 0.01^a	0.05 ± 0.01^b
$\Delta 7$ -Avenasterol [mg/g]	0.08 ± 0.01^c	0.11 ± 0.00^a	0.10 ± 0.05^b
24-Methylenecycloartanol [mg/g]	0.02 ± 0.01^b	0.03 ± 0.00^a	0.02 ± 0.01^b
Total sterols	1.40 ± 0.08^c	1.81 ± 0.01^a	1.61 ± 0.04^b

All values are means of two repetitions with standard deviation

Means within the same row followed by different letters (a,b,c) were significantly different at $p < 0.05$

GSOc: grape seed oil control, GSOm: grape seed oil after microwave pretreatment, GSO r: grape seed oil after roasting pretreatment

Pardo et al. [30] reported that β -sitosterol constituted about 70% of the sterol profile in Spanish GSO, though its concentration was slightly lower (67%) in grape seeds dried at room temperature. They also identified significant amounts of stigmaterol, campesterol, clerosterol, and brassicasterol in ambient temperature-dried grape seed oil. In linseeds, β -sitosterol was the most prevalent phytosterol, followed by campesterol and stigmaterol. Furthermore, roasted linseed oil exhibited higher overall phytosterol content than raw seeds. The highest levels of β -sitosterol (1540.89 mg/kg), cycloartenol (1330.57 mg/kg), campesterol (748.17 mg/kg), and stigmaterol (288.17 mg/kg) were recorded after roasting at 160°C for 8 min.

Other sources, such as *Plukenetia huayllabambana* seed oil, predominantly contained β -sitosterol (60.1 mg/100 g), campesterol (24.8 mg/100 g), and stigmaterol. In walnut oil, β -sitosterol represented over 60% of total phytosterols. The highest levels of β -sitosterol, campesterol, and stigmaterol in walnut oil were observed when the seeds were roasted at temperatures of 140°C, 160°C, and 180°C for 10 min, yielding better results than those obtained with 5 or 15 min of roasting [34].

These findings underscored the impact of thermal pretreatments on enhancing phytosterol content, particularly through microwave treatment, making grape seed oil a valuable source of these beneficial compounds. By optimizing the use of agro-industrial by-products like grape seeds, this approach not only enhanced the nutritional value of the oil but also supported environmental sustainability in the region.

3.5. OXIDATIVE STABILITY BY RANCIMAT TEST

The Rancimat test effectively simulates the oxidation

process of oils, allowing researchers to obtain results in hours that would typically take months or years. The findings indicated that the induction time for GSO decreased as the temperature increased, ranging from 20.97 h at 90°C to 2.32 h at 120°C. According to the Van't Hoff rule, the rate of a reaction typically decreases by two to three times for every 10°C reduction in temperature.

Figure 2 illustrates that the induction time for GSO at 90°C increased after both roasting and microwave pretreatments, rising from 18.09 h to 20.15 h and 20.97 h, respectively. At 120°C, the induction time recorded after both pretreatments was 2.51 h, consistent with findings by Maszewska et al. [35], who reported an induction time of 2.4 h at the same temperature.

Ramos et al. [36] studied the oxidative stability of GSO extracted via cold pressing, followed by filtration and refining. They found higher induction times for GSO at 100°C (15.96 h), 110°C (7.54 h), and 120°C (3.68 h) compared to the current study. The assessment of GSO stability using the Rancimat method remains limited, highlighting the need for further research in this area to understand the oxidative stability of GSO under various conditions.

3.6. KINETIC ANALYSIS OF THE RANCIMAT TEST

The kinetic parameters for GSO oxidation are given in Table IV. The activation energy (E_a) for the tested GSO ranged from 77.49 kJ/mol (untreated) to 79.87 kJ/mol (microwave-treated). These values were in line with those reported by Symoniuk et al. [37] for linseed oils, which ranged from 74.03 to 77.76 kJ/mol. However, higher E_a values were reported by Ramos et al. [36] for grape seed, sunflower seed, and sesame oils, with values of 89.83, 86.58, and 90.37 kJ/mol, respectively. The GSO samples

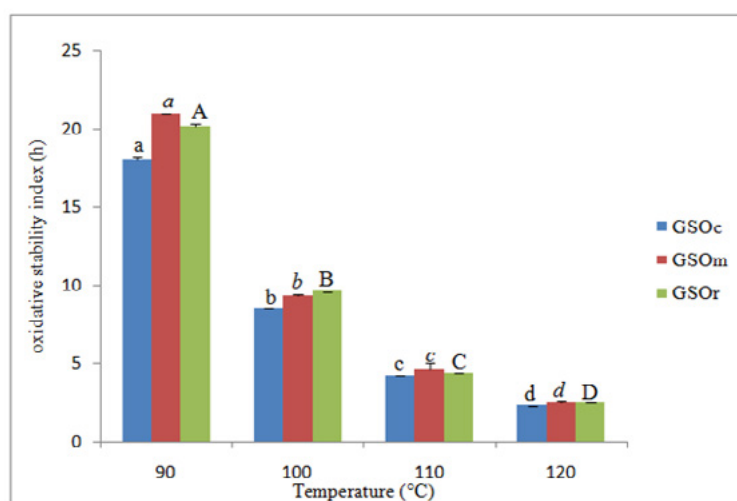


Figure 2 - Oxidative stability of extracted grape seed oils before and after pretreatments

GSOc: grape seed oil control; GSOM: grape seed oil after microwave pretreatment; GSOr: grape seed oil after roasting pretreatment. The small letters (a–d), small italic letters (a–d) and capital letters (A–D) indicate significant differences ($p < 0.05$) between GSOc, GSOM and GSOr, respectively.

Table IV - Calculated values of kinetic parameters of grape seed oil based on Rancimat test

Kinetic parameter	Calculation based on Rancimat		
	GSOc	GSOm	GSO _r
Equation 1			
-a	0.030	0.031	0.031
b	3.923	4.061	4.050
R ²	0.998	0.996	0.996
Equation2			
A	4.256	4.387	4.377
-B	10.469	10.772	10.750
R ²	0.999	0.998	0.997
*E _a	77.488	79.872	79.686
Z	2.94 x 10 ¹⁰	5.91 x 10 ¹⁰	5.62 x 10 ¹⁰
k at 120°C	1.489	1.443	1.453
k at 110°C	0.802	0.763	0.810
k at 100°C	0.418	0.390	0.393
k at 90°C	0.210	0.192	0.194
Q10	1.922	1.961	1.961
ΔH	74.344	76.728	76.542
**ΔS	-122.88	-121.87	-117.39

*E_a, ΔH in kJ mol⁻¹

** ΔS in J molK⁻¹

Z and k in h⁻¹

(E_a): The activation energy was adapted for an isothermal process:

R: the universal gas constant (8.314 J/mol·K).

The equation of rate constant (k) for lipid oxidation of oils:

Q10: the increase in the reaction rate with a 10°C temperature rise

k1 and k2: the rate constants at temperatures T1 and T2, respectively.

The equation of the activation enthalpy (ΔH) and entropy (ΔS):

kB: the Boltzmann constant (1.3806586 × 10⁻²³ J/K)

h: Planck's constant (6.62607556 × 10⁻³⁴ J·s).

GSOc: grape seed oil control, GSOm: grape seed oil after microwave pretreatment, GSO_r: grape seed oil after roasting pretreatment

exhibited relatively low activation energies, which are influenced by their polyunsaturated fatty acid (PUFA) content. According to Adhvaryu et al. [38], a high PUFA content typically decreases E_a, whereas a higher oleic acid content tends to increase it. The substantial presence of PUFAs in GSO implies that less energy is required to initiate oxidation reactions.

The kinetic constant rate (k) of GSO oxidation, shown in Table IV, increased with rising temperature (363.15 K to 393.15 K). High k values indicated rapid lipid oxidation [39]. The oils extracted from grape seeds exhibited the lowest oxidation rates across all temperatures, with k values at 90°C and 120°C being 0.192 h⁻¹ and 1.443 h⁻¹, respectively. The order of lipid oxidation rates was GSOc > GSO_r > GSOm. Factors affecting the k value included fatty acid composition, triacylglycerol structure, and the presence of catalysts or inhibitors [23].

The Q10 number, which indicated how the oxidation rate changes with a 10°C temperature increase, was 1.92 for untreated GSO and 1.96 for both microwave- and roasting-treated GSO. Higher Q10 values suggest that only small temperature variations significantly impact the lipid oxidation rate. Farhoosh and Seyedeh-zohreh [23] reported Q10 values for various oils (canola, soybean, sunflower, corn, and olive) ranging from 2.08 to 2.18, highlighting that Q10 values can vary by oil type. Table IV also includes thermodynamic parameters for lipid oxidation, specifically enthalpy (ΔH) and entropy (ΔS). According to the activated complex hypothesis, reactants must form a thermodynamically stable complex before undergoing reaction. Lower ΔH and ΔS values are associated with slower oxidation rates [19]. The ΔH values ranged from 74.34 kJ/mol (GSOc) to 76.73 kJ/mol (GSOm), while ΔS values ranged from

Table V - Correlation between bioactive compound content of oils, oxidative stability and kinetic oxidation parameters

Quality parameter	OSI at 90°C	E _a	k at 90°C
OSI at 90°C	-	-	-
E _a	0.98 ± 0.13	-	-1.00 ± 0.12
k at 90°C	-0.99 ± 0.09	-0.99 ± 0.01	-
Tocochromanols	0.88 ± 0.05	0.76 ± 0.12	-0.78 ± 0.33
TocopherolsT	0.82 ± 0.11	0.69 ± 0.05	-0.71 ± 0.22
TocotrienolsT3	0.90 ± 0.07	0.80 ± 0.12	-0.82 ± 0.5
Sterols	0.97 ± 0.05	0.90 ± 0.11	-0.92 ± 0.11
SFA	0.98 ± 0.09	0.92 ± 0.09	-0.94 ± 0.33
MUFA	0.97 ± 0.11	1.00 ± 0.33	-1.00 ± 0.53
PUFA	-0.98 ± 0.07	-1.00 ± 0.12	1.00 ± 0.15

OSI: oxidative stability index, E_a: activation energy, k at 90°C: rate constant at temperature at 90°C, SFA: saturated fatty acids, MUFA: monounsaturated fatty acids, PUFA: polyunsaturated fatty acids.

All values are means of three repetitions with standard deviation.

-122.88 J/mol K (GSOc) to -117.39 J/mol K (GSO_r). A positive ΔH indicates an endothermic process for the activated complex's formation, implying that reaction rates increase with temperature. Negative ΔS values suggest the formation of activated complexes, indicating greater oxidative stability [40]. Overall, the oxidative stability and kinetic parameters of GSO varied according to seed pretreatment, primarily due to differences in chemical composition and concentrations of bioactive compounds. The analysis focused on induction time and oxidation rate constant at 90°C due to their variability. Notably, the oxidative stability was highly correlated with sterol content ($r = 0.97$) and fatty acid composition (Table V). Among tocochromanols, tocotrienols significantly influenced oxidative stability ($r = 0.90$). The increase in tocotrienol content from treatments positively affected the activation energy of the oxidation reaction ($r = 0.80$), while decreasing the oxidation rate ($r = -0.82$). These findings aligned with the growing focus on environmental integration in major world regions, where the optimization of agricultural by-products, such as grape seeds, can significantly enhance the sustainability of oil extraction processes. By improving oxidative stability through targeted pretreatment methods, this approach not only improves the quality of GSO but also promotes energy-efficient practices, reducing waste and supporting regions' sustainable agricultural goals.

4. CONCLUSION

In this study, the microwave and roasting pretreatments were applied to grape seed (*Vitis vinifera* L.) prior to oil extraction, resulting in significant changes to the fatty acid composition and an increase in nutraceutical content in the treated oils. The use of the Rancimat accelerated test demonstrated that microwave pretreatment enhanced the oxidative stability of the oil, effectively extending its shelf life. Kinetic parameter analysis further enabled the prediction of oxidation processes under various conditions. The key novelty of this research is its demonstration that microwave pretreatment not only improved the oxidative stability of GSO, but also amplified its nutraceutical properties, offering potential for better-quality oil production. These findings could have broader implications for the agro-industrial sector in all world regions, where optimizing the use of agricultural by-products like grape seeds could support both sustainability and the development of high-value oils with enhanced health benefits.

Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest

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Fatty acids profile, atherogenic and thrombogenic health lipid indices of refined vegetable edible oils and their thermal stability

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In Algeria, olive oil is not available in large quantities, which explains its high price and consequently the use of refined vegetable oils by households for frying. It is well known that, unlike oils extracted from seeds, olive oil has a beneficial effect on health due to its resistance to oxidation. The focus of this paper is two-fold; the first objective is to present the fatty acids (FAs) composition and pro-oxidant heavy metals content of five brands of the most popular Algerian vegetable edible oils, namely: LaBelle, oleor, elio, afia and fleurial. The second objective is to assess their degree of oxidation during heating. The atherogenic and thrombogenic indices were calculated from the FAs composition of the same five Algerian brands of vegetable edible oils. In order to evaluate their oxidative stability, these oils were subject to a Rancimat test and thermogravimetric analysis to calculate activation energy. Our results showed that these oils recorded high polyunsaturated fatty acids (PUFAs) content (mean 60%) and contain pro-oxidant metals (iron and copper). "Feurial" sunflower oil is more sensitive to oxidation than "LaBelle" and "oleor" soybean oils. In fact, sunflower oil, which had the highest PUFAs content (mean 65%) and the highest pro-oxidant copper content (0.058 mg/kg) displayed the lowest induction period (8.27 h) and the lowest activation energy (438.16 kJ/mol) compared to soybean oils (55% PUFAs, 0.004 mg Cu/kg, 12 h and 566 kJ/mol) respectively. The presence of PUFAs at high levels and transition metals even in small amounts enhance the sensitivity of these oil to oxidation during heat processing. Sunflower oil, which is more susceptible to oxidation, should only be used for seasonings.

Keywords: Refined oils; fatty acid composition; heavy metals; oxidative stability; atherosclerosis.

1. INTRODUCTION

Vegetable oils are the most consumed food in the world. In our country, refined vegetable oils are mainly used for frying, cooking and baking because of their lower cost compared to olive oil. These oils have a high nutritional value due to the high content of polyunsaturated fatty acids (PUFAs), especially linoleic acid (18:2, ω 6) [1]. It should be noted that PUFAs found in refined vegetable oils are endowed with nutritional and therapeutic properties. However, these oils are very sensitive to oxidation.

In addition, several factors influence the oxidative instability of edible oils. These include the composition of oil in fatty acids (FA) and the presence of pro-oxidant heavy metals like copper (Cu) and iron (Fe). The rate of oxidation reactions increases with the degree of unsaturation of fats [2]. α -linolenic acid (18:3, ω 3) oxidizes the fastest, followed by linoleic (18:2, ω 6) and oleic acids (18:1, ω 9) [3]. Furthermore, heavy metals in vegetable oils can accelerate oil oxidation even by a very tiny amount by promoting the formation of free radicals from FAs or hydroperoxides [4, 5, 6]. Free radicals in fried foods cause ischaemic heart disease and aging.

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Until now, nothing or little has been known about the content of heavy metals in Algerian edible vegetable oils. This study aims to determine the physical and chemical parameters of the five most consumed brands of vegetable oils in Algeria, for example: FAs profile, free fatty acids (FFA) content, atherogenic, thrombogenic and peroxide indices and iodine value (IV). Moreover, this research was carried out in order to shed light on the oxidative stability of the same five brands of Algerian vegetable edible oils, such as: the Rancimat test and calculating the energy of activation using thermogravimetric analysis.

2. MATERIALS AND METHODS

2.1. REFINED OILS STUDIED

One litre bottles of each of the five most consumed brands of Algerian vegetable edible oils were purchased in a local supermarket, namely: fleurial, La-Belle, oleor, elio and afia with a shelf life of two years. The five bottles were kept in the fridge at 4°C until subsequent analyses.

It should be noted that fleurial is a pure sunflower oil, whereas LaBelle and oleor are pure soybean oils. Conversely, elio and afia are blended oils and are prepared by blending soybean and sunflower oils at a ratio of 80:20 for the first oil and the blending of soybean with corn oils at a ratio of 95:5 for the second oil. Both the physical and chemical characteristics of these oils were determined; each oil was analyzed in triplicate.

2.2. PHYSICAL PARAMETERS ANALYSIS

2.2.1 Fatty acid analysis

The FA composition of the five brands of Algerian vegetable edible oils was determined by gas chromatography (GC) in order to evaluate the content of PUFA that are sensitive to the oxidation process. The presence of two double bonds in the FA structure causes faster oxidation than with a single double bond.

The FAs composition of the samples was determined as fatty acid methyl esters (FAMES). FAMES were obtained by the transesterification of edible oils with BF₃-MeOH after alkaline hydrolysis [7]. 1 mg of the vegetable oil sample and 500 µL of C17 were mixed with 1 mL of 0.5N methanolic NaOH, and the mixture was saponified at 70°C for 15 minutes. After cooling to room temperature, 1 mL 14% BF₃-MeOH solution was added and the mixture was heated at 70°C for 10 minutes to promote the formation of the methyl ester. Again, the mixture was cooled to room temperature followed by the addition of 6 mL of distilled water and 2 mL of pentane. The solution was allowed to settle until two layers were formed, and the supernatant was collected and transferred into GC vials and frozen at -20°C prior to analysis. FAMES were analyzed GC-MS using an Agilent 7890A gas chromatograph

system equipped with a flame ionization detector. Separation was performed on a capillary fused silica column (30 m × 0.25 mm). The stationary phase consisted of 80% biscyanopropyl and 20% cyanopropyl-phenyl while hydrogen was used as a carrier gas. The temperature was set at 45, 195, 220 and 240°C for 2, 7, 2 and 2 minutes respectively for a total duration analysis 21.9 minutes. The injector and temperature detector were maintained at 220 and 280°C, respectively. The results were expressed as percentage of identified FAs.

2.2.2 Atherogenic and thrombogenic index

The polyunsaturated/saturated (P/S) ratio considerably influences the occurrence of coronary heart disease. However, this parameter has been replaced by indices of atherogenicity and thrombogenicity [8].

The atherogenic and thrombogenic indices (A.I. and T.I.) were calculated from the FAs composition of the five brands of Algerian edible oils according to the following equations, described in a previous study [9].

$$AI = \frac{C12:0 + 4 \cdot C14:0 + C16:0}{\sum AGMI + \sum AGPI_{\omega 6} + \sum AGPI_{\omega 3}}$$

$$AI = \frac{C14:0 + C16:0 + C18:0}{0,5 \cdot \sum AGMI + 0,5 \cdot \sum AGPI_{\omega 6} + 3 \cdot \sum AGPI_{\omega 3}}$$

where C12:0, C14:0, C16:0, C18:0, ω3 and ω6 are lauric, myristic, palmitic, stearic, linoleic and linolenic acids, respectively.

2.2.3 Pro-oxidant heavy metals content

Trace metals in refined vegetable oils may originate from the soil and fertilizers, or from contamination during processing and storage. The presence of small amounts of trace metals in oils and fats is known to negatively affect oil quality. The strongest and most notable pro-oxidants are copper and iron, which produce a significant oxidative effect at concentrations as low as 0.005 and 0.03 ppm respectively [10].

In our study, the measurement of heavy metals in fresh refined vegetable edible oils was carried out using a Perkin Elmer PINAACLE 900F graphite flame atomic absorption spectrometer. Results obtained are expressed in mg per kg of oil. Previously, a calibration curve was drawn using increasing known concentrations of heavy metals.

To establish the calibration curve for the determination of heavy metals (iron and copper) in oil samples by Atomic Absorption Spectroscopy (A.A.S.), 1 mL of reference solution (1000 ppm) was transferred to a 100 mL volumetric flask and filled to the mark with distilled water to form the stock solution (100 ppb). From the latter, 1 mL was transferred to a 100 mL volumetric flask and filled to the mark with

double-distilled water. Lastly, 40 μ L of each solution underwent spectrophotometry, which automatically established the calibration curve. For the determination of heavy metal in oils studied by A.A.S., 3 g of the oil studied was placed in a graphite oven (MAB-FM74) at a gradually increasing temperature of 25-500°C (2°C/min) in order to allow the slow charring of the sample until all the carbon had been removed. To the cooled ash, a 5 mL aliquot of HNO₃ (60%) was added to promote dissolution. A nitric acid solution was filled to 10 mL and diluted 10 times. Finally, 50 μ L were injected in a graphite tube for analysis; the results were displayed automatically. All reagents used were of analytical-reagent grade.

2.3. CHEMICAL PARAMETERS ANALYSIS

The six brands of Algerian edible oils were chemically characterized according to the AFNOR method [11].

2.3.1 Free fatty acid content

The FFAs are one of the chemical parameters that impact considerably on the quality of edible oils. These molecules turn oil rancid. Rancidity is the unpleasant odour and that develops spontaneously in oils. There are two type of rancidity: hydrolytic and oxidative. Acid value (AV) is a measurement of the FFAs content in the oil. The higher the AV, the higher the level of FFAs, which translates into lower oil quality. During refining, FFAs are very carefully removed because they promote oxidation, thus fully refined edible oils become less prone to oxidation. The percentage of FFAs is the amount of potassium hydroxide expressed in milligrams required to neutralize the FFAs present in one gram of fat or oil. FFAs content was determined according to the method of [11].

2.3.2 Peroxide index

The peroxide value (PV) of oil samples was measured according to the method of [11]. This technique is based on iodometric titration that quantifies iodine produced from potassium iodide by peroxides present in oil. The results were expressed as milliequivalents of active oxygen per kilogram of edible oil. PV highlights the extent of primary oxidation and is a key indicator of oil quality and potential rancidity.

2.3.3 Iodine value

The I.V. indicates the degree of unsaturation of edible oils. It is defined as the number in grams of iodine absorbed by 100 g of oil. The I.V. value was determined using method [11].

2.4. OXIDATIVE STABILITY

In this investigation, the Rancimat test and calculation of activation energy were used in order to compare the thermal oxidation stabilities of the five brands of refined oils.

2.4.1 Rancimat measurement

The Rancimat analyses served to evaluate the oxidative stability of oils and the latter was expressed as the oxidative induction period expressed in hours and defined as the duration of oil's natural resistance to oxidation, due to the presence of naturally occurring antioxidants which delay oxidation during frying [12]. Rancimat tests of all the samples were performed according to the method of [13] with 743 Rancimat apparatus (Methrom AG, Herissau, Switzerland). It should be noted that 3 g of oil was weighed in the reaction vessel and heated at 98°C under a constant air flow (10 L/h). The induction times were printed automatically by the apparatus software with an accuracy of 0.005. All analyses were carried out in triplicate and the mean value was recorded.

2.4.2 Calculating activation energy

Thermal deterioration of the oils due to lipid oxidation can be also examined by thermogravimetric analysis (T.G.A.). The oxidation process in oil was assessed by monitoring mass change (gain or loss) as a function of temperature or time [14, 15]. In this study, the thermogravimetric analyses of oils were carried out using «NETZSCH STA 449C» apparatus. TGA involves heating oil samples of 2-5 g from 20°C to 500°C, under a constant air flow (25 mL/min) and constant heating rates. Activation energies (E_a) were calculated by means of Arrhenius equations. Activation energy is the minimum energy required to start oxidation reaction. Therefore, it is an indicator of thermal stability and degradation behaviour of edible oils.

2.5. STATISTICAL ANALYSIS

Statistical analyses were performed with The Stat. Box software. The data were analyzed by one-way analysis of variance (ANOVA), and the means were compared by the least significant difference (LSD) test at a significance level of 0.05.

3. RESULTS AND DISCUSSION

3.1. REFINED VEGETABLE OILS CHARACTERISTICS

Refined vegetable oils are cheaper than olive oil, which makes them a popular choice among Maghreb households with low purchasing power. In Algeria, olive oil is expensive, costing 10 Euros/L, so the majority of the population cannot afford it. Conversely, refined sunflower oil is prized by a large segment of the Algerian population in salad dressings, not only because it is cost-effective, but it also contains many added synthetic vitamins as A, D and E. Moreover, sunflower oil does not impart any new flavour when used for seasoning salads, thereby maintaining the unique flavour profile of leafy vegetables.

3.2. LEVELS OF PHYSICAL PARAMETERS

The results regarding the physical parameters of the five most consumed brands of Algerian vegetable edible oils are shown in Table I. The physical parameters are within the official ranges for these oils as specified in the Codex Alimentarius [16].

3.2.1 Fatty acids composition

Table I shows that there were significant differences between the five brands of edible oils in terms of FAs composition. The content in saturated fatty acids (S.F.As.) ranged from 10.959% in “fleurial” (pure sunflower oil) to 15.331% in “LaBelle” (pure soybean oil). In addition, palmitic acid (C16:0) was the major SFA in all our oils, followed by stearic acid (C18:0). The percentage of palmitic acid was the lowest in “fleurial” oil (6.472%) and the highest in “LaBelle” oil (10.624%). Our results regarding total SFAs are in accordance with those reported by Zambiasi et al [17]; Tasan et al. [18]; Kostik et al. [19]; Kaur et al. [20]. As they pointed out, soybean oils are more saturated compared to sunflower oils; the values obtained were respectively 15.10 v.s 12.36%, 14.24% v.s 9.45%, 13.5% v.s 8.8% and 16.34% v.s 10.62%. Consequently, they suggest that soybean oil may be more resistant to thermal oxidation than sunflower oil. Furthermore, our oil samples did not contain lauric acid. These results are in line with Gregorio [21] and Gopala et al. [22], who revealed that only coconut oil is a major source of lauric acid C12:0. However, these values were lower than those found by Asgary et al. [23] in Iranian edible

oils (18.9%).

“Fleurial” oil exhibited the lowest content in mono-unsaturated fatty acids (M.U.F.A.) acids (24.117%), whereas “LaBelle” oil displayed the highest content in MUFAs (29.763%). “LaBelle” oil had the highest oleic acid (28.055%) content, while “Afia” (blended oil) registered the lowest content in oleic acid (20.977%). Our results regarding total content in MUFAs are not in accordance with those obtained by Kaur et al. [20]. Our pure “fleurial” sunflower oil (24.117%) was not as rich in MUFA as sunflower oil analyzed by Kaur et al. [20], who reported (37.40%). However, our soybean oils were richer in MUFAs in comparison with Indian soybean oils [20].

“LaBelle” oil showed the lowest content in polyunsaturated fatty acids (P.U.F.A) at (54.565%), whereas “fleurial” oil displayed the largest PUFA content (64.769%). Linoleic acid (C18:2, ω 6) was the major PUFA present in all analyzed oils : “fleurial” oil (64.442%), “LaBelle” (49.366%). Unlike linoleic acid, an average amount of α -linolenic acid was found in “Afia” oil (6.376%) vs. (0.327%) in “fleurial” oil. “Fleurial” oil contains a low proportion of SFAs and a considerable quantity of MUFAs (84.378%) as well as a maximum level PUFAs (88.886%), which gave it a higher unsaturated FAs (HUFAs) content than the other analyzed pure soybean oils.

Our results regarding the MUFA and PUFA content of our edible oils are not in accordance with those of Kaur et al. [20]. Pure “fleurial” sunflower oil was richer in PUFAs than Indian sunflower oil, which contained

Table I - Fatty acids composition of studied refined vegetable oils

Fattyacids (% w/w)	Marks of oils				
	'LaBelle'	'Oleor'	'Elio'	'Afia'	'Fleurial'
C14:0	0.080±0,000 ^a	0.080±0,000 ^b	0.070±0,000 ^d	0.070±0,000 ^c	0.070±0,000 ^e
C16:0	10.611±0,016 ^d	10.637±0,003 ^c	8.050±0,001 ^e	10.749±0,012 ^b	6.472±0,008 ^f
C18:0	3.984±0,0016 ^c	3.919±0,000 ^d	3.517±0,000 ^f	4.493±0,003 ^b	3.857±0,004 ^e
C20:0	0.423±0,003 ^b	0.432±0,002 ^a	0.288±0,002 ^e	0.358±0,000 ^d	0.273±0,001 ^f
C24	0.201±0,001 ^c	0.202±0,003 ^c	0.213±0,002 ^b	0.124±0,002 ^e	0.245±0,005 ^a
C18:1, ω 9	28.055±0,030 ^a	27.184±0,012 ^b	23.537±0,002 ^c	20.977±0,003 ^e	23.266±0,004 ^d
C18:1, ω 7	1.458±0,002 ^a	1.441±0,006 ^b	1.059±0,003 ^e	1.335±0,001 ^c	0.699±0,002 ^f
C18:2, ω 6	49.366±0,020 ^f	50.240±0,027 ^e	60.475±0,002 ^b	55.063±0,007 ^c	64.442±0,043 ^a
C18:3, ω 3	5.199±0,003 ^d	5.297±0,001 ^c	2.320±0,000 ^e	6.376±0,000 ^b	0.327±0,001 ^f
C20:1, ω 9	0.250±0,001 ^b	0.266±0,006 ^a	0.173±0,003 ^e	0.183±0,001 ^d	0.152±0,001 ^f
Σ SFA	15.331±0,023 ^c	15.281±0,013 ^d	12.188±0,000 ^e	15.797±0,010 ^b	10.959±0,016 ^f
Σ MUFA	29.763±0,033 ^a	28.891±0,012 ^b	24.769±0,002 ^c	22.495±0,003 ^e	24.117±0,005 ^d
Σ PUFA	54.565±0,023 ^f	55.537±0,028 ^e	62.795±0,003 ^b	61.439±0,007 ^c	64.769±0,042 ^a
P / S	3.560±0,006 ^f	3.633±0,004 ^e	5.150±0,001 ^b	3.890±0,004 ^c	5.909±0,013 ^a
ω 6 / ω 3	9.494±0,004 ^c	9.474±0,005 ^c	26.060±0,000 ^b	8.630±0,000 ^d	195.271±0,121 ^a
A.I.	0.1296	0.1297	0.0951	0.1314	0.0759
T.I.	0.2660	0.2639	0.2347	0.2644	0.2297

SFA: saturated fatty acids; MUFA: monounsaturated fatty acids; PUFA: polyunsaturated fatty acids; P / S: PUFA / SFA; AI: atherogenic index; TI: thrombogenic index

Means $\pm$ SD (standard deviation) within a row with the same lower case letters are not significantly different at $p < 0.05$

only 51.23% of linoleic acid. However, our soybean oils contained less PUFAs than Indian soybean oils (59.27%) and (53.58%) of linoleic acid [20]. Finally, all soybean oils had similar α -linolenic content.

The relationship between SFAs and PUFAs content is expressed as the P/S index. Table I reveals that all analyzed vegetable oils displayed higher total PUFAs content than SFAs content. These oils had a P/S ratio that varied from 3.560 for "LaBelle" oil to 5.909 for "fleurial" oil. Moreover, all refined vegetable oils marketed in Algeria are highly unsaturated. "Fleurial" oil had high PUFAs (C18:2, $\omega 6$ + C18:3, $\omega 3$) content (64.769%) with linoleic acid being the major FA (64.442%) and α -linolenic acid the minor one. It is clear that oils with high content are more prone to oxidation. Oil source, plant genotype, environmental conditions - particularly temperature- and water supply considerably influence FAs composition.

3.2.2 Atherogenic and thrombogenic index

The atherogenicity Index (A. I.) explains the relationship between the sum of the main SFAs and the main classes of unsaturated fatty acids (UFAs). The thrombogenicity Index (T.I.) explains the tendency of blood cells to form clots in the blood vessels due to the adhesion of lipids with blood cells. SFAs are pro-atherogenic : they promote their adhesion to cells in the circulatory system and are pro-thrombogenic. Conversely, UFAs are anti-atherogenic : they inhibit the clotting of blood cells and they are anti-thrombogenic : they prevent the appearance of coronary diseases [24, 25].

Pareira et al [9] developed two very useful equations, one for calculating the index of thrombogenicity (T.I.) and another for calculating the index of atherogenicity (A.I.). Indices of atherogenicity and thrombogenicity of the five brands of Algerian edible refined oils are summarized in Table I. Note that the T.I. was 0.2297 for "fleurial" (pure sunflower oil), and 0.2660 for "LaBelle" (pure soybean oil). In contrast, for A. I. the values were 0.0759 for "fleurial", and 0.1296 for "LaBelle". Our results regarding atherogenic and thrombogenic indices of Algerian refined edible oils are in agreement with those reported by Kaur et al. [20], who worked on refined Indian soybean and sunflower oils. However, the values were very low, when compared to those of olive oil ; 0.14 and 0.32 respectively for A.I. and T.I. [8]. A.I. and T.I. values were the lowest in sunflower oil (0.07 and 0.21) and the highest in soybean oil (0.13 and 0.27). However, "elio" oil (blended soybean and sunflower oils at a ratio of 80:20) showed a significant decrease in both indices, thereby revealing a lower risk of developing coronary diseases [24, 25]. Indeed, Mennoti et al. [26] pointed out that there is a positive and highly significant correlation between A.I. and T.I. and the mortality rate from coronary heart disease.

They also observed a direct link with all-cause mortality at 25 and 50 years of age.

In addition, A.I. and T.I. provide very useful knowledge about the impacts of SFAs, MUFAs and PUFAs in the development of coronary heart diseases [27,9]. Some FAs have a greater role in atherosclerosis, while others play a key role in thrombogenesis. Palmitic acid has a cholesterol-raising effect and is therefore considered as atherogenic SFAs, while stearic acid influences clot formation in blood vessels and is known as thrombogenic SFAs [27]. C14:0, C16:0 and C18:0 contents in our oils were similar to those obtained by Kaur et al. [20]. The myristic acid is considered to be four times more atherogenic than palmitic acid.

MUFAs and PUFAs in edible oils considerably reduce the atherogenic and thrombogenic effects. PUFAs are more prominent in preventing atherosclerosis and thrombogenesis than MUFAs [8]. There were significant differences between our sunflower oils and Indian sunflower oils in terms of MUFAs and PUFAs fractions. Pure Algerian "fleurial" sunflower oil showed the lowest MUFAs content compared to Indian sunflower edible oils, and "fleurial" oil had a higher PUFAs content than its Indian counterpart. MUFAs and PUFAs are represented respectively by oleic and linoleic acids. However, Ng et al. [28] pointed out that edible oils heated repeatedly many times have potentially adverse health effects and are responsible for the occurrence of atherosclerosis. In contrast, phenolic compounds, which occur naturally in small quantities in fresh edible oils, exert an antioxidant effect ; heating oils over and over again destroys and eliminates the antioxidant properties of these substances. Consumption of deep-fried foodstuffs alters the physiology and vasorelaxation of the endothelium [29].

3.2.3 Heavy pro-oxidant metals content

As is shown in Table II, there were significant differences between Algerian edible oils in terms of heavy metals content. Our results were in agreement with the Codex Alimentarius [16], 1.5 mg/kg oil for iron and 0.1 mg/kg oil for copper. The iron levels in the analyzed oils were 0.047 in "elio", 0.049 in "fleurial", 0.066 in "oleor", 0.070 in "Afia" and 0.082 mg/kg in "LaBelle" oils. The copper concentrations were 0.0010 mg/kg in "oleor", 0.007 in "LaBelle", 0.023 in "Afia", 0.031 in "elio" and 0.058 in "fleurial" oils. Soybean oil displayed the lowest copper levels, while sunflower oils exhibited the highest concentrations of copper.

Copper is an essential nutrient for the human body. Together with iron, it enables the formation of red blood cells. It helps maintain healthy bones, blood vessels, nerves, and the immune system, and it contributes to iron absorption. Copper and iron are required in our diet. Biologically, these two heavy

minerals exhibit a wide range of functions. Iron is involved in numerous processes necessary for normal bodily functions: oxygen transport, oxidative phosphorylation, metabolism of neurotransmitters, and DNA synthesis all require iron. Iron deficiency is prevalent in most of the developing world; the main cause is a diet low in bioavailable iron [30]. Copper is responsible for structural and catalytic properties of multiple enzymes necessary for normal bodily functions [31]. This metal is required for infant growth, host defence mechanisms, bone strength, red and white cell maturation, iron transport and brain development [32]. Anaemia, neutropenia, and bone abnormalities (osteoporosis, fractures, etc.) are the main symptoms of copper deficiency. Other effects described include hypopigmentation of the hair and skin, hypotonia, impaired growth, increased incidence of infections and altered immunity [32, 33]. However, a high content of PUFAs, copper and iron in edible oils triggers oxidation [34, 35].

The presence of heavy metals in our refined vegetable oils might be due to crude oil imported by our country and/or introduced during the refining carried out locally. The values were higher than those reported by Pehlivan et al., [36] who worked on Turkish sunflower oils (mean 0.00918 mg/kg oil). Finally, Acar [37] found 1.52 and 1.51 mg/kg of copper and iron in Turkish soybean and sunflower oils respectively.

Algerian oils had lower concentrations of iron compared to their Nigerian, Iranian, Spanish and Chinese counterparts : Nnorom and Ewuzie [38] in Nigeria recorded 50-425 mg/Kg, while Farzin and Moassesi [39] in Iran measured 17.66 µg/g and Garrido et al. [40] in Spain found 0.27-1.31 µg/g sunflower oil and 0.38-0.76 µg/g soybean oil. Finally, Zhu et al. [41] in China obtained 27.3-29.8 and 21.6-23.1 µg/g of sunflower and soybean oils respectively.

The values of iron content in Algerian edible oils were higher than those reported by Pehlivan et al. [36] for Turkish sunflower oils (0.01652 mg/kg oil), while Acar [37], who worked on the same Turkish brands, obtained 0.07 mg/kg sunflower oil and 0.09 mg/kg soybean.

Furthermore, Algerian edible oils contain less copper than their Nigerian, Iranian, Spanish and Chinese counterparts : Nnorom and Ewuzie [38] in obtained

0.22-4.99 mg/kg, while, Farzin et al. [39] in Iran found 0.25 and 0.18 µg/g for sunflower and soybean oils respectively, whereas Garrido et al. [40] in Spain recorded 0.03-0.19 µg/g and 0.04-0.12 µg/g for sunflower and soybean oils respectively, while Zhu et al [41] in China reported 0.052-0.068 and 0.048-0.056 µg/g of sunflower and soybean oils respectively. Finally, Dugo et al. [42] in Italy found 0.1068 and 0.67458 mg/kg for sunflower and soybean oils respectively.

3.3. CHEMICAL PARAMETERS LEVELS

The results regarding the chemical parameters of the five most consumed brands of Algerian vegetable edible oils are shown in Table II. The FFAs content was lowest in the blended oil "elio" (0.044) and the highest in the percentage of FFAs was the pure sunflower oil "LaBelle" (0.054). The minimum PV was observed in pure "fleurial" sunflower oil (1.61 meq/kg), whereas the maximum PV was found in pure "LaBelle" soybean oil (2.00 meq/kg). There were no significant differences ($p \geq 0.05$) between the five brands of Algerian vegetable edible oils in terms of IV.

On one hand, AV measures FFAs in oil. Normally, FAs occur in form of triglycerides (TGs), however, during processing the FAs may get hydrolyzed into FFAs. The higher the AV found, the higher the level of FFAs, which translates as decreased oil quality. Acceptable levels for all oil samples must be below 0.6 mg KOH/g (measured in potassium hydroxide per gram) and 0.3% (as oleic acid) [16]. Therefore, according to edible oil specifications, all five brands of Algerian edible oils fell within the acceptance range.

On the other hand, IV measures of the degree of unsaturation in oil TG. The greater the IV, the more unsaturation and the higher the susceptibility to oxidation. The Codex Alimentarius [16] established IV at 118-141 for sunflower oil and 124-139 for soybean oil. Therefore, according to these specifications, all the five brands of oils were within the set ranges. IV is an indicator oil unsaturation, which is the most important analytical characteristic of oil [43].

PV reflects the freshness of the oil. As with FFAs, all five brands of Algerian edible oils were in compliance with the specifications in terms of PV. The latter provides useful knowledge regarding the level of lipid oxidation, and must not exceed the upper limit (10

Table II - Physical and chemical properties of studied refined oils

	Marks of oils				
	'LaBelle'	'Oleor'	'Elio'	'Afia'	'Fleurial'
Free fatty acids (%)	0.054±0.003 ^a	0.051±0.003 ^a	0.044±0.003 ^b	0.050±0.001 ^a	0.051±0.005 ^a
Peroxide value (meq kg ⁻¹)	2.00±0.20 ^{bc}	1.97±0.12 ^{bc}	1.70±0.20 ^c	1.85±0.10 ^b	1.61±0.21 ^a
Iodine value(g 100g ⁻¹)	127.05±2.07 ^a	124.07±4.10 ^a	125.14±4.82 ^a	126.25±4.03 ^a	129.91±2.78 ^a
Copper content (mg/kg)	0.007±0.001	0.0010±0.000	0.031±0.001	0.023±0.001	0.058±0.001
Iron content (mg/kg)	0.082±0.001	0.066±0.001	0.047±0.001	0.070±0.001	0.049±0.001

meqO₂/kg) established by [16]. So, the greater the PV, the higher the rate of oxidation of the oil [44].

Malondialdehyde is an organic compound formed during lipid peroxidation. It is a biomarker of oxidative stress: a high level of this by-product indicates greater fat degradation and causes oxidative damage in cells and tissues. The urinary excretion of malondialdehyde and lipophile carbonyl compounds has been observed in animals and humans [45].

The peroxydes impair the physiological function of the blood vessels endothelium and consequently negatively affect the amount of nitrogen monoxide (NO) ; this molecule plays a key role in maintaining cardiovascular homeostasis, thanks to its impact on blood vessels dilatation [46, 29]. In addition, studies have shown that consumption of oxidized fats causes carcinogenesis [47]. It should be noted that fat peroxydes, once absorbed, cause the formation of other fat peroxydes by chain reaction. Furthermore, induced oxydative stress stimulates the production of pro-inflammatory cytokines [48]. However, fresh food intake provides protection of the blood vessels structure. In fact, many researchers demonstrated that polyphenols ingested simultaneously with oxydable foods prevent fat oxidation in the stomach. These molecules break down the oxidation chains of membrane phospholipids [49].

Vitamins and minerals are contained mainly in plant foods like fruits, vegetables and cereals and are endowed with antioxidant properties, considerably reducing the peroxydation and inflammation that occur during digestion [49, 50, 51]. The amount of oxydated lipoproteins diffused in the blood circulation plummets substantially, providing the best state of health to consumers.

Note that fried foods should be accompanied with green vegetables since the latter are rich in antioxidant molecules which, on one hand, reduce the number of free radicals in the digestive tract and, on the other hand, at low levels in the body, reactive oxygen molecules are useful and play an essential role in the mechanism of cell signalling, thereby contributing to maintaining cell homeostasis [52].

It is almost impossible to prevent oxidation in edible oils. However, it is possible to influence the kinetics of the reaction, slow down the speed at which this reaction occurs and delay this phenomenon considerably. In the past, our grandparents filtered soybean oil after frying and incorporated slices of green apples into

the cooled oil before storing it in sealed containers in dark cupboards. When frying, they also introduced a raw peeled carrot into the oil in order to regulate its temperature and keep it clean. Current research has shown that apple polyphenols neutralize and reduce the concentration of polar compounds that occur during frying. Finally, current research emphasises the effect of high temperatures on advanced oil degradation.

Antioxidants found in fresh fruits and vegetables increase the physiological capacity of the human organism to release free radicals outside the body, and thereby sustain the function of endothelium. Introducing a slice of raw apple in used cooking oil enables its reuse, thanks to the phenolic compounds that sequester the free radicals that are formed during frying. A large amount of lipoperoxydes is harmful and a risk factor in cardiovascular diseases [49].

In Algeria, edible oil is packaged in non-inert plastic bottles, yet plastic packaging may contain chemicals that can dissolve in edible oil and contaminate it. However, the frequency of fried food consumption exceeds the recommendation of only twice a week so the new trend means that the risk of oil contamination by chemicals from plastic packaging is eliminated since the oil is consumed before chemicals can build up in the oil.

3.4. THERMAL STABILITY EVALUATION

The results from the Rancimat test and the calculation of activation energy of the five brands of Algerian vegetable edible oils are summerized in Table III.

3.4.1 Rancimat test

The Rancimat test is an easy method for determining the induction time of lipid oxidation. Several parameters impact the Rancimat test such as sample quantity, air flow rate and temperature [53]. Induction time is the time that the hydroperoxides produced by oil oxidation take to decompose [54]. The Rancimat induction time at 98°C for the five brands of edible oils varied from 8.27 h to 14.05 h; pure "fleurial" sunflower oil displayed minimum oxidative stability, while pure soybean oil "oleor" had maximum thermal stability. "LaBelle" required a relatively short induction time (10.15 h), while the blended oils ("elio": 80% soybean + 20% sunflower oil and "afia": 95% soybean + 5% corn oil) were characterized by a longer induction time (14.05 h and 13.46 h) respectively.

Table III - Stability index of studied refined vegetable oils

	Marks of oils				
	'LaBelle'	'Oleor'	'elio'	'Afia'	'Fleurial'
Induction time (h)	10.15	14.05	13.46	13.25	8.27
Activation energy (kJ/mol)	550.09	581.52	570.50	570.03	438.16

Furthermore, pure soybean oil "oleor", characterized by a high induction time, was more stable than pure "fleurial" sunflower oil with a low induction time. "Fleurial" oil recorded a shorter induction period, higher IV and higher copper content than "oleor", confirming that "fleurial" was highly sensitive to oxidation. There were significant differences between "LaBelle" and "oleor" oils in terms of induction times. These differences were due to the variations in copper content. "LaBelle" oil had a higher copper concentration than "oleor" oil. Therefore, "oleor" oil was thermally more stable and more resistant to oxidation. The sensitivity of "fleurial" oil to oxidation is due to its high PUFA content, large copper concentration and short induction time.

3.4.2 Activation energy

Thermogravimetric analysis evaluates the oxidative and thermal stability of edible oils by detecting the mass change of the related oil sample through thermal degradation [15]. Activation energy represents the minimum energy required to start the first step of thermal decomposition and the beginning of FAs decomposition; the higher the activation energy, the harder it is for a reaction to occur and vice versa. This is expressed in kilojoules per mole (kJ/mol). Our results with regard to the activation energy of the five oils are summarized in Table III. The results regarding activation energy of the five brands of Algerian oils were in line with the results of the Rancimat test. Note that activation energy values ranged from 438.16 kJ/mol for pure "fleurial" sunflower oil to 581.52 kJ/mol for pure "oleor" soybean oil.

The content of FAs and the presence and concentration of heavy metals (copper and iron) considerably influence oil activation energy. Our data established the order in terms of the thermal stabilities of the five oils as follows: oleor > elio > Afia > LaBelle > fleurial. On one hand, "fleurial" oil exhibited the lowest activation energy among the five oils due to having the highest content in PUFAs and pro-oxidants (copper). On the other hand, refined pure "oleor" soybean oil displayed the highest activation energy and therefore the slowest oxidation due to its lower copper content. In fact, copper accelerates hydrogen peroxide decomposition to a speed 50 times faster than ferrous ion (Fe²⁺), and ferrous ion speeds up this thermal degradation reaction to 100 times faster than ferric ion (Fe³⁺) [55]. In addition, copper increases the rate of oil oxidation due to the reduction of the activation energy of the initiation step in auto-oxidation down to 63~104 kJ/mol [56]. Indeed, the rate of the formation of the primary oxidation products increases as the amount of PUFAs and pro-oxidant metals in oils rises. Finally, these transition metals catalyze the decomposition of hydroperoxides and lead to more rapid formation of undesirable substances [36].

4. CONCLUSION

In this study, physical, chemical and oxidative stability analyses of the five top most consumed Algerian vegetable edible oils were conducted in order to assess their thermal stability. Our results showed that these five edible oils are within the acceptance range of the physical and chemical parameters described in the Codex Alimentarius. The five brands of oils behaved differently in terms of thermal degradation and oxidative stability characteristics. Based on the Rancimat test and thermogravimetric analysis, our data showed that pure "fleurial" sunflower oil is the most prone to thermal degradation and oxidation because of its high content in PUFAs and heavy metals (copper and iron). Conversely, pure "oleor" soybean oil and "LaBelle" are the most thermally stable due to their low concentrations in copper and iron. The blended oils "elio" and "Afia" displayed intermediate values of thermal and oxidative stabilities because they are produced by mixing sunflower and soybean oils at different ratios. Finally, in order to improve the thermal and oxidative stability of pure "fleurial" sunflower oil, the full-refining of this oil is recommended in order to get rid of all FFAs, and any heavy metals (copper and iron) while adding stabilizers like olive oil polyphenols.

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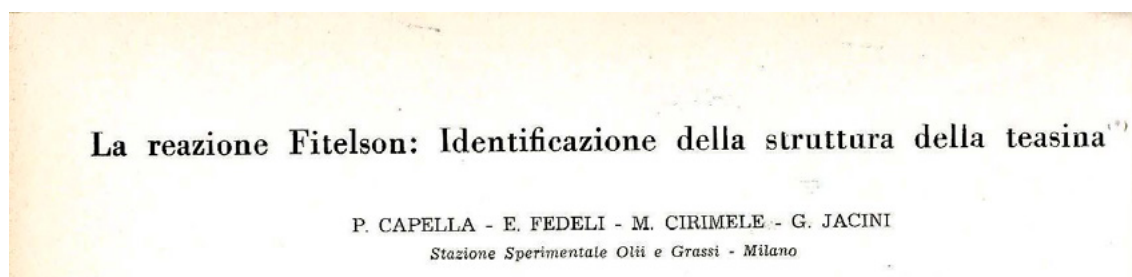
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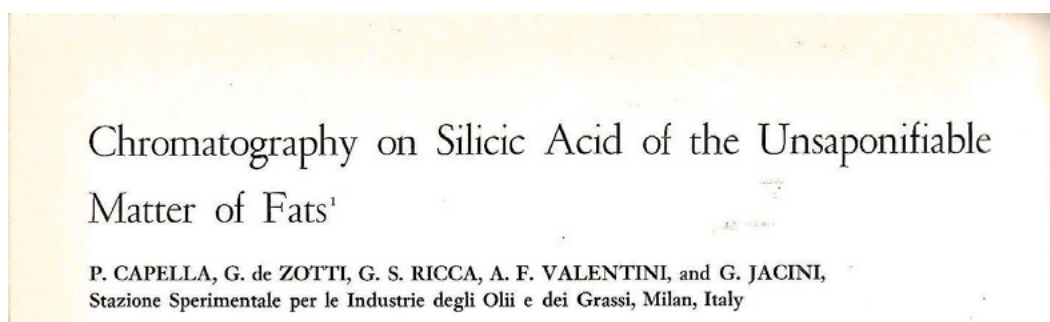
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Pubblicazioni del passato commentate alla luce delle conoscenze odierne

Alcune storiche esperienze italiane sull'analisi dei componenti minori degli oli vegetali



La Rivista Italiana delle Sostanze Grasse, vol XL, 296 (1963)



The Journal of the American Oil Chemists' Society, vol 37, 564 (1960)

Una nota di

Lanfranco Conte e Paolo Bondioli

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L'analisi delle sostanze grasse, finalizzata alla verifica della purezza e della qualità ha vissuto una prima fase denominata "Chimica degli indici" in cui si effettuavano test ponendo la sostanza in esame in determinate condizioni e valutando se si comportasse come sostanze note, sia come aspetto fisico (es. formazione di precipitati), sia come aspetto cromatico, mediante lo sviluppo di determinate colorazioni, ma rimanendo in genere nel campo delle reazioni cromatiche e non colorimetriche. L'intensità della colorazione in genere non seguiva le leggi della spettrofotometria e il risultato era valutato in termini di POSITIVO/NEGATIVO, il primo talvolta preceduto dall'avverbio DEBOLMENTE.

La Tabella 1 riporta alcuni esempi di questi test; desideriamo qui porre l'attenzione sulla reazione, o test, di Fitelson per la ricerca dell'olio di the. Si tratta in questo caso di un interessante punto di congiunzione tra la "Chimica degli indici" e l'applicazione delle tecniche separative, cromatografiche ed in particolare gas cromatografiche, il cui sviluppo ebbe grande impulso nei primissimi anni '50, e che videro come campo applicativo di elezione, l'analisi dei lipidi. James e Martin [1] sono riconosciuti come inventori della gas cromatografia, nel 1952 descrissero la separazione degli acidi grassi da formico a dodecanoico. In seguito, Orr e Callen [2] svilupparono la separazione dei metil esteri di una serie molto più ampia di acidi grassi, con particolare attenzione ai C18 poliinsaturi.

Tabella 1 - Esempi di "Chimica degli indici" [3,4]

Anni	Test	Significato
1860-1870	Titolo degli acidi grassi	
	Numero di Henner	Acidi grassi "fissi" insolubili in acqua
1870-1890	Numero di acidità	Acidi grassi liberi
	Numero di Saponificazione	Quantità di acidi grassi
	Indice di Reichert-Meissl- Polenske	Acidi grassi fissi e volatili
1890-1920	Numero di Iodio	Numero di doppi legami
	Numero di Acetile	Numero di gruppi -OH
	Reazione di Heydenreich	Ricerca di olio di Colza, Mais, Mandorle
	Hauchecorne Reazione di Brullé	
	Numero di Kirchner	Quantità di acidi grassi volatili
	Indice di Bömer	Ricerca di grasso suino
	Metodo di Fahrion	Acidi grassi ossidati
1920-1940	Indice di Bellier	Differenziazione oli di oliva vs oli di semi o grassi animali
	Indici A e B	Sansa vs oliva vergini
	Indice di perossidi	Rancidità
	Numero di tiocianogeno (solfocianogeno)	Grado di insaturazione
	Test di Kreiss	Rancidità
	Stamm Test	Rancidità
	Test di Fitelson	Ricerca di Olio di the
	Reazione di Halphen	Ricerca di Olio di cotone
	Reazione di Villavecchia	Ricerca di Olio di sesamo
	Grado termo solforico	Ricerca di oli "siccativi"
	Indice di Maumenè	Analisi mediante acido solforico [5] Citato per olio di papavero [6]
	Reazione di Tortelli & Ruggeri	Ricerca di olio di arachide (Acido Lignoceric)

Capella et al nel 1963 [7] intrapresero una ricerca per identificare il o i composto/i responsabili della positività alla reazione di Fitelson, in considerazione, come si legge sotto, dei dubbi sollevati sulla sua attendibilità.

Sono note le polemiche suscitate dalla applicazione della reazione di Fitelson alla ricerca di adulterazione di olio di oliva mediante olio di thè. Alla base di queste polemiche sta senza dubbio l'assoluta empiricità della reazione. Infatti fino ad ora, pur essendo state studiate a fondo le condizioni migliori per condurre la reazione, nulla si sapeva circa la (o le) sostanze responsabili della reazione stessa. Né si sapeva se le sostanze Fitelson-positivo dell'olio di thè e dell'olio di oliva fossero o meno la stessa sostanza.

Dato il notevole interesse merceologico assunto da questa reazione, da alcuni anni presso la Stazione Sperimentale Olii e Grassi abbiamo iniziato una ricerca allo scopo di identificare la sostanza responsabile della reazione di Fitelson dell'olio di thè e di chiarire se tra la sostanza presente in alcuni olii di oliva — Fitelson-positivi — e la sostanza presente nell'olio di thè ci fosse identità o meno.

Tutta questa attenzione nei confronti dell'olio di semi di the (*Camelia sinensis*) può apparire strano al lettore dei nostri giorni, tuttavia al tempo, in considerazione dell'elevatissimo contenuto in acido oleico di questo olio e delle limitate potenzialità diagnostiche dei sistemi di controllo la commistione era tutt'altro che impossibile. Il saggio di Fitelson era realizzato aggiungendo cloroformio, anidride acetica e acido solforico al campione in esame. L'aggiunta provoca la formazione di una intensa colorazione fluorescente verde alla luce riflessa e bruna alla luce trasmessa, che diviene intensamente rossa per aggiunta di etere etilico anidro, quindi leggermente bruna. L'olio di oliva e gli altri oli commestibili mostrano un colore verde, mentre l'olio di semi di the, se presente, genera un colore rosso per aggiunta dell'etere etilico. L'olio di the si può ottenere per estrazione dei semi con una resa in olio che può raggiungere il 42%. Le poche notizie sulle sue caratteristiche sono riportate nel classico volume di Martinenghi (8): numero di iodio 77-81 (g I₂/100 g), numero di saponificazione 188-196 (mg KOH/g), insaponificabile 0,2-0,3%, principali acidi grassi saturi (11%), oleico (87%), linoleico (2%), massa volumica (15°C) 0,916-0,917, indice di rifrazione (20°C) 1,4691-1,4779.

Non deve essere infine confuso con il Tea Tree Oil (Malaleuca oil), olio essenziale non edibile estratto dalle foglie di *Malaleuca alternifolia*.

Già nel 1960, sempre Capella et al [9] avevano ottenuto il frazionamento dell'insaponificabile di diversi oli vegetali utilizzando una colonna cromatografica impaccata con silica gel ed avevano evidenziato la presenza di un composto tipico dell'olio di the, denominato "teasina", che risultò positivo al test di Fitelson e che era presente nella frazione degli alcoli terpenici.

This paper describes the isolation of unsaponifiables from fats and oils and the separation of this material into various components by elution chromatography on silicic acid columns. The elution is performed by a series of solvents or mixtures of solvents of increasing polarity and permits the quantitative isolation of the following series of components: The saturated hydrocarbons; the polyene hydrocarbons (squalene); the waxes; the esters of sterols; the aliphatic alcohols; a group of materials the nature of which will make up a separate paper, containing triterpene alcohols; the free sterols; and a group of substances still unidentified which may be alteration products.

Although the method was developed to study the unsaponifiables of extracted olive oil, it may also be applied to other fats and oils. The resolution of unsaponifiables containing compounds of a different chemical type from those listed will, of course, depend upon the functional group of the compounds, and application of the elution scheme will, in general, permit their separation. As an example of this, in the separation of teaseed oil unsaponifiables (Figure 7), we have isolated by our method a group of substances giving the so-called Fitelson reaction (11).

La cromatografia su carta evidenziò che in realtà nella frazione positiva al test di Fitelson erano presenti almeno 2 sostanze, come confermato dall'analisi gas cromatografica (Fig 1 del presente articolo, fig. 3 dell'articolo del 1963)

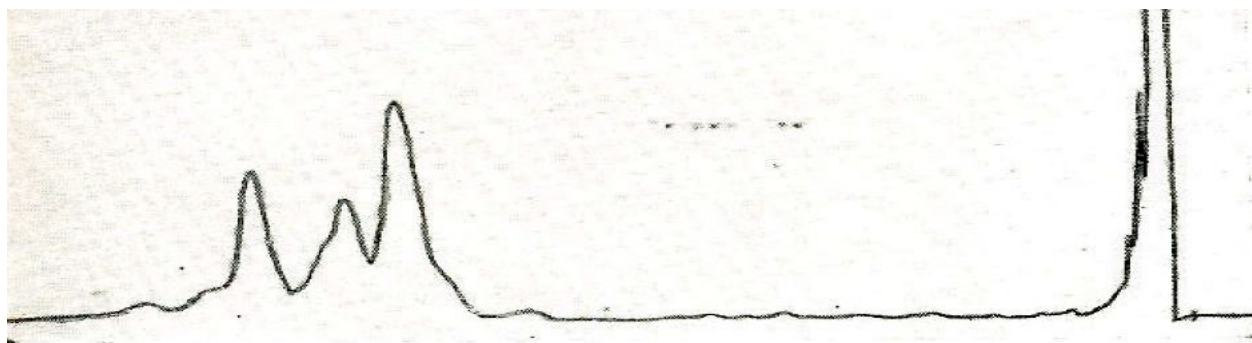


Fig. 1 (Fig 3 /1963): Analisi gas cromatografica della frazione positiva al test di Fitelson

A questo punto, per un ulteriore approfondimento della natura di questi composti, venne intrapresa una classica strada della chimica preparativa applicata alle sostanze naturali, come riportato nel seguente paragrafo:

Cromatografando su colonna di allumina la miscela dopo acetilazione è stato possibile separare dalle frazioni di coda un acetato fondente a 235-237° che è stato successivamente identificato come acetil- β -amirina (I) in base all'analisi elementare, al potere rotatorio specifico e allo spettro I.R. Inoltre un campione autentico

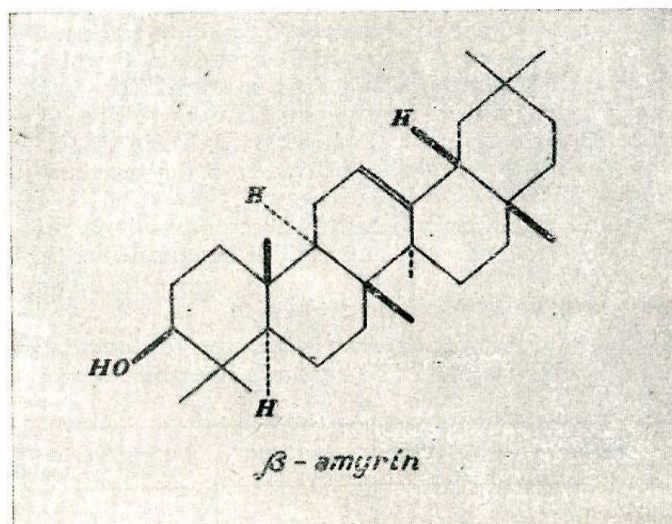


Figura 4

di β -amirina (Fig. 4) mostrò avere un tempo di ritenzione in gascromatografia uguale a quello del picco maggiore della miscela di triterpeni dell'olio di thè.

La β -amirina così purificata fu sottoposta al test di Fitelson che inaspettatamente risultò negativo! Gli Autori quindi proseguirono le indagini sulle altre frazioni:

Controllando la reazione di Fitelson sulle diverse frazioni della cromatografia degli acetati avevamo potuto constatare che le frazioni di testa davano una reazione più intensa delle frazioni di coda.

Abbiamo allora ripetuto più volte la cromatografia degli acetati raccogliendo ogni volta le teste e ricromatografandole separatamente.

Infine per cristallizzazione frazionata delle frazioni prive di β -amirina, dopo aver allontanato tracce di un alcool alifatico superiore, si è isolato un altro acetato con punto di fusione 140-141°C, che in gascromatografia dava un solo picco, con tempo di ritenzione uguale a quello del secondo picco della miscela grezza.

Va messo in evidenza il laborioso metodo seguito, tipico della operatività delle ricerche di allora che portò alla identificazione del burirrospermolo come "responsabile" della positività al test di Fitelson

Questo composto mostrava nettissima la reazione di Fitelson. L'identificazione di questa sostanza ci è stata facilitata da alcune considerazioni.

Innanzitutto un campione di cicloartenolo in nostro possesso e proveniente da lattice di una euforbicea dava una Fitelson nettamente positiva, mentre il cicloartenolo puro che abbiamo identificato tra gli alcoli triterpenici dell'olio di lino (3) non dà assolutamente la Fitelson.

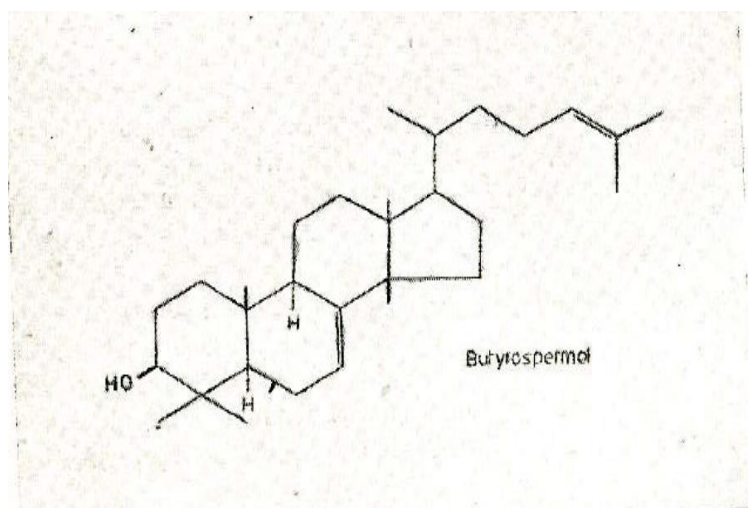
Avevamo constatato che l'insaponificabile del burro di karité dà una Fitelson molto intensa. E' anche noto che nelle euforbiacee sono contenuti alcuni alcoli triterpenici della serie dell'eufano quali l'eufolo e l'eufobolo e che, d'altra parte, dal burro di karité è stato isolato da Halsall un altro alcool triterpenico di questa serie, il butirospermolo.

Confrontando i dati chimico-fisici della teasina con quelli dei triterpeni della serie dell'eufano si può constatare che corrispondono perfettamente con quelli riportati per il butirospermolo (tabella 1).

TABELLA 1

	Teasina	Eufolo	Butirospermolo	Tirucallolo	Eufobolo
p. f.	142	109	146,5-147,5	163,5	121-122 124-125
Analisi	+ 6,1	+ 41	+ 11	- 17	± 0
C	82,3	82,0	82,0	82,0	82,1
trov. H	11,3	teor. 11,1	11,1	11,1	11,2

A questo punto, una volta identificato il composto suscettibile di reattività al test di Fitelson, gli Autori si interrogano sul perché essa sussista e ragionando sulla formula di questo componente, riportata da una loro figura:



Notarono che a differenza degli altri alcoli, esso presenta una catena laterale orientata in α , anziché in β , come avviene in tutti gli altri terpeni, tale caratteristica è comune all'eufenolo, anch'esso positivo al test.

Era quindi lecito ipotizzare che la "teasina", ritenuta responsabile della positività del test di Fitelson fosse il butirrospermolo, così come ogni altro terpene con catena laterale in 17 in configurazione α .

Un'ulteriore riflessione sulla osservata positività al test di Fitelson di alcuni oli d'oliva, indusse però i ricercatori a considerare la positività al test come concentrazione dipendente, ovvero, poiché piccole concentrazioni di alcoli terpenici e non di solo butirrospermolo sono presenti negli oli d'oliva, la osservata "leggera positività" sarebbe potuta dipendere dalla inferiore concentrazione di butirrospermolo in questi ultimi rispetto agli altri oli, ma anche dalla presenza di altri componenti non identificati nel corso di questo studio.

Il lettore avrà notato come in questo lavoro si sia posto l'accento su una classe di composti della frazione insaponificabile il cui studio fu in seguito piuttosto negletto, a parte alcuni articoli di Rutkowski et al (1966) [10], Itoh et Al (1974, 1981) [11,12] e di Lercker et Al (1981) [13], a favore della frazione degli steroli. le esperienze "storiche" della ricerca italiana su questa classe di composti saranno oggetto di una seconda nota.

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British manufacturer of handcrafted, air-dried pet food and treats seek international partners for commercial cooperation

Ref. BOGB20250929008

A UK-based pet food producer offers premium air-dried food and treats for dogs and cats. Products are made with British meats and vegetables, gently dried to preserve nutrients. The company seeks commercial agreements with distributors and retailers abroad.

Deadline 29 September 2026

Patent-licensed process for transforming carob seed germ into a high-protein food – available for licensing and technical cooperation

Ref. TOES20250929020

A company from Mallorca (Spain) offers a license for a patented process that transforms carob seed germ into Manduca®, a clean-label, high-protein food ingredient with over 60% protein content. The company is looking for food producers, agricultural cooperatives, or carob processors interested in diversifying their activities through this scalable and sustainable innovation.

Deadline 2 October 2026

Polish distributor of professional cosmetic ingredients seeks international partners (distributors or manufacturers) to expand their portfolio on the Polish market

Ref. BOPL20251014002

A well-established Polish distributor of cosmetic ingredients for skincare, haircare, and personal care formulations is looking for new international suppliers. The company offers strong market presence, scientific expertise, and flexible cooperation under distribution exclusivity contract to introduce high-quality raw materials to Poland's cosmetics sector.

Deadline 14 October 2026

Romanian manufacturer specialized in custom stainless steel conveyor systems for the food and beverage industry seeks commercial part-

nerships with equipment integrators, resellers, and end-users across Western and Northern Europe

Ref. TORO20250627001

Romanian manufacturer with over 25 years of experience and more than over 45% turnover from export, specialized in custom stainless steel conveyor systems for the food and beverage industry. Also active in sectors such as airport logistics, e-commerce, stainless steel conveyor systems, and intralogistics. Seeks commercial partnerships with equipment integrators, resellers, and end-users across Western and Northern Europe.

Deadline 15 October 2026

Italian public research institute is looking for partners to develop new vegetable rennets for the production of vegetarian and vegan cheeses.

Ref. TOIT20251021013

Italian public research institute is developing new vegetable rennets for the production of vegetarian and vegan cheeses. The institute is looking for industrial partners interested in: developing these vegetarian and vegan products or proceeding to industrial scale-up; developing and characterizing new products.

Deadline 21 October 2026

Innovation cluster from the East of Spain, representing companies along the entire packaging value chain, is interested in participating as a partner in international projects

Ref. TOES20251029005

Innovation cluster representing more than 100 companies in the packaging value chain from the East of Spain is interested in participating as a partner in international projects. It includes firms working with paper, cardboard, plastic, and wood, supplying industries such as food, automotive, and ceramics.

The cluster can play a role in testing and developing technologies and solutions within its member companies, in the results dissemination, and in the overall visibility within the ecosystem.

Deadline 29 October 2026

A Ukrainian producer of equipment for extraction and processing of vegetable oils is looking for long-term cooperation with partners from EU under the manufacturing agreement

Ref. BOUA20251104004

The Ukrainian manufacturing company specializes in the manufacture of equipment for the oil-and-fat industry. The company seeks for foreign partners (preferably from the EU) to establish long-term partnerships and implement its export potential. Cooperation is possible under the subcontracting and manufacturing agreement.

Deadline 4 November 2026

Sustainable valorisation of agro-food waste rich in lignin.

Ref. TOES20251203014

A research group from a Spanish university has developed a patented sustainable method to extract high-purity lignin from agro-food residues, such as coconut husk, using deep eutectic solvents (DES) combined with ultrasound. The process achieves ≥80% extraction yield in reduced time and is suitable for producing bio-based raw materials used for various industrial applications: chemical, pharmaceutical, cosmetic...

Deadline 3 December 2026

French SME develops innovative natural liquid food/feed supplements derived from plants (herbs, algae...) on a white label basis, and offers its services to formulate, manufacture or package food supplements in aseptic conditions

Ref. TOFR20260109005

French SME specialises in formulation of organic liquid food supplements, extraction without chemical solvents and packaging without heat treatment, preservatives or additives in glass ampoules (5-15mL), bottles (20mL-1L) or sterile bags (10-1000L). It offers services to brands willing to expand their range with finished products, manufacturers looking to add natural active ingredients to their processes or looking for a service provider to aseptically package their products in ampoules/bottles.

Deadline 9 January 2027

Portuguese company of organic essential oil and vegetable oil offers raw materials for cosmetics, personal care, perfumery, detergents and pharmaceutical applications under commercial (agents or distributors) or supplier agreements

Ref. BOPT20260218014

A company with production sites in Angola and Portugal specialized in the supply of organic essential and vegetable oils, high-quality raw materials tailored to the cosmetics, personal care, perfumery, detergents and pharmaceutical applications is seeking for B2B partners to establish long-term commercial partnerships, appointing agents or distributors, as well as supplier agreement. Leveraging a strategic warehouse in PT, it ensures efficient distribution within the European market.

Deadline 18 February 2027

Indian Supplier of 100% Pure Essential Oils for Cosmetics, Aromatherapy and Natural Product Manufacturers Seeks EU Industrial Buyers

Ref. BOIN20260324023

An Indian manufacturer of 100% pure therapeutic-grade essential oils and carrier oils is seeking cosmetics manufacturers, aromatherapy brands, perfumery companies, and natural product manufacturers across the European Union interested in sourcing high-quality botanical oils in bulk quantities. The company offers reliable supply, competitive manufacturing capabilities, and long-term cooperation opportunities under bulk supply or manufacturing agreements.

Deadline 24 March 2027

Sustainable bio-fermented lipid actives for cosmetic formulations

Ref. TOEE20260407019

ÄIO is an Estonian biotechnology company developing sustainable, fermentation-derived lipids from renewable sidestreams for skincare and body care applications. Its ingredients include RedOil, a carotenoid-rich oil positioned for hydration and skin renewal benefits, and ZymaLipid Complex, a purified fatty-acid blend supporting emollience, barrier-feel, and formulation stability. The company is seeking partners for their biotech ingredients.

Deadline 8 April 2027

Danish scaleup seeks production partners in Europe to produce UHT high protein drinks with a combination of dairy and plant ingredients

Ref. BRDK20260407034

A Danish company working in the dairy business seeks a partner in Europe to produce UHT protein drinks in a recycled PET bottle solution with screw cap and sleeve. The products are intended for sales in Scandinavia and potentially more northern European countries. The company has already several customers interested in a protein drink product range. Estimated productions volumes for a range of 2-3 recipes in 330ml PET are: Yr 1: 300mT per recipe (min. 2 recipes at launch) Yr 2: 500mT per recipe.

Deadline 7 April 2027

Per ricevere ulteriori informazioni e per entrare in contatto con i soggetti titolari degli annunci si prega di inviare una mail a: simpler@mi.camcom.it specificando il codice progetto di interesse.

Enterprise Europe Network (EEN)

È la rete nata nel 2008 per volontà della Commissione Europea con l'obiettivo di supportare l'innovazione, il trasferimento tecnologico e l'internazionalizzazione di piccole e medie imprese ed enti di ricerca.

Si avvale di oltre 600 organizzazioni presenti in 60 paesi e offre un sistema integrato di servizi gratuiti per aiutare le imprese a individuare nuovi partner commerciali, produttivi e tecnologici all'estero; per promuovere la partecipazione ai programmi Europei per la ricerca, come Horizon Europe, e per fornire gli strumenti utili per essere più competitivi sui mercati internazionali, migliorando la conoscenza dei mercati e della legislazione europea.

In Lombardia i servizi di Enterprise Europe Network sono garantiti da **Simpler** (Support Services to IMProve innovation and competitiveness of businesses in Lombardia and Emilia-Romagna), di cui Innovhub SSI è partner.

Come ti può aiutare la rete EEN?

Far crescere l'azienda e sostenere l'internazionalizzazione:

- Informazioni sulla legislazione EU
- Informazioni e assistenza sul Regolamento REACH
- Ricerca di finanziamenti a supporto delle imprese
- Supporto per l'individuazione di opportunità commerciali all'estero
- Sostegno per lo sviluppo di nuovi prodotti o processi

Sviluppare partneriati:

- Supporto alla partecipazione a brokerage event e company mission e per la conclusione di accordi di trasferimento tecnologico
- Assistenza nella ricerca partner

Implementare processi di innovazione e trasferimento tecnologico:

- Servizio di analisi delle capacità di gestione e miglioramento dell'innovazione
- Supporto al trasferimento tecnologico/open innovation
- Informazione su bandi di finanziamento e supporto alla partecipazione a programmi di ricerca
- Pre-screening delle proposte progettuali EIC Accelerator

I servizi della rete EEN sono gratuiti.

Per cercare il tuo partner in Europa, consulta il nostro database: <https://een.ec.europa.eu/partnering-opportunities>

Per maggiori informazioni contattare:

Federico Agostini

federico.agostini@mi.camcom.it



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RECENSIONI DI LIBRI

PRONTUARIO DEGLI ALIMENTI PER IL SUINO 115 SCHEDE PER VALUTARE LE MATERIE PRIME

A CURA DI:
DANIELE CEVOLANI



V Edizione - 2025
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libri.edagricole@newbusinessmedia.it
www.edagricole.it

Come le precedenti, questa quinta edizione si prefigge di aiutare allevatori e tecnici a formulare un'alimentazione oculata in funzione del benessere animale, della qualità delle carni e dei parametri qualitativi richiesti dall'industria dei salumi e dal mercato delle carni, con particolare attenzione alle strategie per la riduzione degli antibiotici e al sostegno naturale della salute animale.

Il "Dizionario" degli alimenti" conta 115 schede di valutazione di materie prime prese in esame per descrivere pregi e difetti, qualità e caratteristiche, valori nutrizionali e prerogative dietetiche.

Oltre alle materie prime classiche sono state aggiunte schede di valutazione di alimenti del futuro (proteine animali processate, alghe e prodotti derivati, farine d'insetti ecc.) ed additivi e coadiuvanti di recente immissione sul mercato.

INDICE:

Introduzione - Acidificanti - Acqua di bevanda -

Additivi e coadiuvanti tecnologici - Aminoacidi - Aromatizzanti: esaltatori di aroma e gusto - Enzimi - Esempi pratici di formulazione - Fabbisogni nutrizionali - Fabbisogni nutritivi di alcuni ibridi commerciali - Granulometria dei mangimi per suini - Micotossine - Minerali - Oli essenziali ed estratti di erbe - Piani di razionamento - Probiotici e lieviti - Vitamine - Materie prime ad alto tenore in amido e/o zuccheri - Materie prime ad alto tenore in fibra - Materie prime ad alto tenore in lipidi - Materie prime ad alto tenore proteico - Materie prime liquide - Tabella riassuntiva dosaggi materie prime - Alimentazione e gestione delle scrofe iperprolifiche - Alimentazione del suino durante il periodo estivo - Alimentazione del suino biologico - Alimentazione e benessere del suino - Alimentazione ed impatto ambientale - Disciplinare alimentare del suino italiano destinato alle produzioni "DOP e IGP" - Strategie nutrizionali per la riduzione degli antibiotici - Principali patologie alimentari o ambientali del suino - Software per l'alimentazione e la gestione dell'allevamento - Sostanze indesiderabili.

AUTORE:

Daniele Cevolani, Agronomo e Nutrizionista, autore di libri e pubblicazioni sull'alimentazione degli animali da reddito.

CON LA COLLABORAZIONE DI:

Marianna Altieri | Monica Battini | Valentino Bontempo | Roberto Bombardieri | Alessandro Galli | Silvana Mattielloe | Matteo Rizzi | Michelangelo Taina.

MALATTIE DELLE API E SALUTE DEGLI ALVEARI

A CURA DI:

ALBERTO CONTESSI, GIOVANNI FORMATO



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Pagine 468

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e-mail: libri.edagricole@newbusinessmedia.it

www.edagricole.it

Il cambiamento climatico, la diffusione di patogeni, parassiti e predatori esotici, l'utilizzo scorretto di pesticidi, le pratiche agricole intensive e in generale un ambiente sempre più ostile hanno creato per le api una situazione di costante emergenza che deve essere affrontata mediante corrette pratiche gestionali e veterinarie. Saper gestire una situazione come quella descritta presuppone competenze, acquisibili con una costante azione di formazione ed aggiornamento degli addetti ai lavori.

In questo libro vengono affrontati in modo chiaro ed esauriente i principali aspetti della biologia e della patologia delle api, come individui e soprattutto come alveare.

Oltre alla tradizionale suddivisione delle patologie tra malattie parassitarie, batteriche, virali e fungine, senza trascurare i predatori, si è cercato di esporre la materia in base a criteri di rilevanza, sfruttando le novità della ricerca in fatto di eziologia e di tecniche diagnostiche.

Un'aggiornata appendice normativa fornisce le necessarie informazioni su tutte le norme che, a vario titolo, interessano il settore.

Gli autori si rivolgono alle migliaia di apicoltori operanti in Italia, ma anche ai tanti veterinari, sia operanti nel privato sia nei Servizi veterinari pubblici, che stanno assumendo un ruolo sempre più importante in apicoltura, oltre al personale tecnico degli Enti coinvolti e agli studenti che si avvicinano a questa materia.

INDICE:

Biologia ed organizzazione sociale delle api - La gestione delle api allevate: buone pratiche e misure di biosicurezza - I predatori - Malattie parassitarie di maggior rilevanza - Malattie di natura batterica di maggior rilevanza - Malattie di natura fungina di maggior rilevanza - Malattie di natura virale di maggior rilevanza - Malattie di minor importanza - Intossicazioni ed avvelenamenti delle api - Piante tossiche per le api - Sindrome dello spopolamento degli alveari - Normativa sanitaria di riferimento.

AUTORI:

Alberto Contessi è un biologo, specializzato in fitopatologia ed esperto in apidologia. Ha diretto per dieci anni il Servizio Fitosanitario della Regione Emilia-Romagna, e per sei anni è stato Presidente dell'Osservatorio Nazionale Miele. È coordinatore del Tavolo tecnico dell'Intesa nazionale apicoltura/agricoltura e Direttore Responsabile del "Notiziario dell'Apicoltore". È autore del volume *Le Api. Biologia, allevamento, prodotti*. Si occupa di apicoltura da oltre quarant'anni.

Giovanni Formato è docente di Apidologia nel corso di Medicina Veterinaria dell'Università di Roma Tor Vergata. Specializzato in Ispezione degli Alimenti di Origine Animale, esperto in apidologia e patologie delle api, lavora presso l'Istituto Zooprofilattico Sperimentale del Lazio e della Toscana, dove ha diretto il Laboratorio di Apicoltura, il Centro di Riferimento FAO su salute delle api, sicurezza dei prodotti dell'alveare e antibiotico-resistenza e il Centro di Collaborazione WOAHA sulle buone pratiche apistiche e la biosicurezza. Coordina numerosi progetti nazionali e internazionali. Collabora con APIMONDIA e l'Associazione di Apicoltori Europea (EBA).

..... CONGRESSI

Advanced Technologies in Oilseed Processing, Edible Oil Refining and Oil Modification. 34th Practical Short Course.

1-2 June | Ghent, Belgium

This 1.5-day short course will bring together industry experts from around the world offering practical information on oilseed and oil processing and quality issues and how to integrate these in downstream products. The program is directed at plant engineers, chemists, technicians, managers, and superintendents. This is a unique opportunity for new plant personnel and for those who are experienced to meet experts in the field to discuss current problems and learn how to enhance their operations. The course material will also serve as a useful reference for processors, product formulators, chemists and technicians as well as business managers familiar with oils & fats processing, and the production of finished products.

Target Group:

Decision makers such as technicians, equipment manufacturers, product formulators, plant engineers, processors, chemists and sales and marketing specialists.

EARLY BIRD - By May 7, 2026

See more information:

<https://smartshortcourses.com/34thoilsandfats/>

4th Lipid Droplets Oleosomes Conference

2-4 June | Montpellier, France

During this event lipid droplets and oleosomes, their parts and potential applications as functional assemblies from plants to health and disease including nutritional and cosmetics innovations will be discussed.

The event will take place in Campus La Gaillarde located in the School of Agronomy Campus, close to the City Center, in the heart of the MedVallée and very nearby Montpellier University of Science and organized in tight connections with CIRAD and University.

Info: <https://4thldocongress.seminaire.inrae.fr/>

2026 IGC Grains Conference

Charting the future drivers of global grains trade

9-10 June | London, UK

The 2026 IGC Grains Conference will cover a wide range of crucial topics, including the impact of a low market price environment on future supply and demand, risk management, and innovation in logistics. The organisers aim to look ahead to the opportunities and challenges facing the agribusiness sector as it makes strategic decisions, with a special focus on Southeast Asia.

The Conference is an in-person event and will be held on Tuesday 9 and Wednesday 10 June 2026 at the IET, London: Savoy Place, 2 Savoy Place, London WC2R 0BL.

The 4th High-Level Dialogue between producing and importing countries will focus on efforts in the Middle East and Africa to strengthen food system resilience, with particular emphasis on the role of trade.

As part of a series of related industry events under the banner "London Grains Week", the 2026 IGC Grains Conference is a truly global platform for dialogue between policymakers and operators across the entire value chain.

Take part in two full days devoted to discussions on the challenges, risks, and opportunities in global trade in grains, oilseeds, pulses, and related sectors.

You will have a unique opportunity to access global operators in the grains sector and take advantage of multiple networking opportunities, including a cocktail reception on the evening of 9 June.

More information:

<https://www.igc.int/en/conference/confhome.aspx>

12th International Deep-Frying Symposium

18-19 June | Hamburg, Germany

Over the years, the International Symposia on Deep-Frying have established a unique platform for dialogue between food producers, foodservice and restaurant operators, research scientists, official and commercial laboratories, regulators, suppliers, and consumers. The goal has always been to foster scientific exchange and translate research findings into practical applications.

Deep-frying remains one of the most popular and efficient methods of food preparation worldwide.

Over recent decades, extensive research has improved our understanding of fat degradation mechanisms, oil absorption, and heat and mass transfer during deep-frying. This knowledge has enabled the development of strategies to enhance product quality, extend the usable life of frying oils, and improve the overall efficiency and sustainability of frying processes. Since a significant portion of the frying medium is absorbed by the food, understanding oil degradation and its potential impact on human health remains a key topic.

Technological advances—including improved frying equipment, more effective filtration systems, and the development of new frying media—have further contributed to better oil stability and product quality. At the same time, sustainability considerations are increasingly shaping the entire frying process, from oil selection to waste management.

While concerns about trans-fatty acids have diminished due to regulatory and consumer-driven changes, other heat-induced contaminants remain under scrutiny, including acrylamide, 3-MCPD and glycidyl esters, as well as emerging topics such as chloroparaffins, MOSH, and MOAH.

A crucial aspect of assessing frying oil and fried food quality is sensory analysis. Previous symposia have emphasized that sensory quality is one of the most important criteria for evaluating frying oils and products. Therefore, one objective of this symposium is to familiarize participants with sensory evaluation approaches, complemented by practical insights into their application.

The technical program of the 12th International Symposium on Deep-Frying will cover all relevant aspects of the frying process, including analytical and sensory methods, safety and quality evaluation, and innovative approaches to improve oil and product performance. The symposium is intended for professionals involved in fried food production, research, quality control, regulation, and related fields, as well as all those with a general interest in deep-frying.

The aim of the symposium is to provide participants with up-to-date knowledge and to discuss current and future challenges in deep-fat frying. Over two days, the symposium will offer a comprehensive overview and a solid scientific basis for the

production of high-quality, safe, and sustainable fried foods.

More information:

<https://veranstaltungen.gdch.de/microsite/index.cfm?l=11921&modus=>

FATS-O-MICS: Workshop on Food Lipids and Lipidomics for Health, Nutrition, and Sustainability

02-03 July | Averio, Portugal

The event aims at bringing novel insights and addressing emerging challenges in the exciting field of food lipids and lipidomics, with a vision for healthier diets and a more sustainable future.

This meeting brings together a diverse community of scientists, young researchers, stakeholders, and industry experts.

Key topics:

- The importance of lipids and lipidomics in human health and sustainable diets,
- The development of alternative food sources,
- The integration of food analysis with traceability systems, and
- The analytical challenges associated with the characterization and quantification of lipids in complex food matrices.

Workshop sessions:

- Session 1: Analytical Challenges in the Diversity of Food Lipids
- Session 2: Food Lipids and Lipidomics: From Molecules to Nutrition and Health Insights
- Session 3: Lipids and lipidomic in Food Quality, Safety & Traceability
- Session 4: Alternative and new sources of lipids, sustainability and future directions

These challenges are both technical and strategic, requiring interdisciplinary approaches that combine analytical chemistry, food science, nutrition, biotechnology, and data science.

More information and updates:

<https://veranstaltungen.gdch.de/microsite/index.cfm?l=11918&modus=>

27th International Symposium on Plant Lipids

5-10 July | Malaga, Spain

This meeting will offer an opportunity to share recent advances in the field of plant lipid biology, as their roles in development, stress responses, signalling, and biotechnological applications.

The scientific program will feature a series of highly engaging and diverse talks, reflecting the dynamic and rapidly evolving nature of lipid research.

Beyond the scientific content, the meeting will provide a unique setting to exchange ideas, foster collaborations, and strengthen the connections within our international community.

The welcoming atmosphere, together with the outstanding location and facilities in Málaga, will create the ideal environment for meaningful scientific dialogue and interaction.

The scientific program of the congress will be structured around sessions showcasing the latest advances across the diverse areas that make up the field of plant lipids.

The program also includes keynote talks highlighting the most impactful recent discoveries, as well as the most remarkable contributions from young researchers.

- Fatty acid and glycerolipid synthesis
- Extraplastidial lipids: Plant sphingolipids and sterols
- Triacylglycerol metabolism and lipid droplets
- Plastidial and algal lipids
- Lipid trafficking and membrane contact sites
- Surface lipids
- Lipid signaling
- Emerging methods and lipidomics
- Plant lipids and stress response
- Plant Lipid Biotechnology

Stay tuned for upcoming updates:

<https://ispl2026malaga.com/ISPL2026>

National Seminar on Palm Oil Milling, Refining, Environment and Quality (POMREQ 2026)

11-12th August | Sarawak, Malaysia

The Seminar is an established national seminar series supporting the continuous development of the Malaysian palm oil industry. The seminar will showcase recent advancements in milling technologies, including the practical applications of AI in palm oil mills to enhance operational efficiency and product quality. Sessions will also address progress in refining technologies, renewable energy utilisation, biomass valorisation and sustainability practices. POMREQ 2026 brings together industry leaders and technology innovators to shape a smarter, more competitive and sustainable future for the palm oil processing sector.

Objectives:

- To share updates on technological improvements that enhance productivity and efficiency in palm oil milling and refining;
- To highlight recent research and innovations that improve product quality and environmental performance;
- To discuss key issues and challenges affecting the palm oil industry;
- To provide a platform for knowledge exchange, networking and collaborations among industry stakeholders.

Visit:

<https://mpob.gov.my/2026/03/national-seminar-on-palm-oil-milling-refining-environment-and-quality/>



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Author instructions

La Rivista Italiana delle Sostanze Grasse (RISG) welcomes research, experimental or technological papers, short communications, reviews articles on edible and industrial oils and fats of vegetable and animal origin, soaps, detergents, surfactants, cosmetics and toiletries, mineral oils, lubricants.

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